A. P. HOWES
Publisher

M. D. REESER
Advertising Manager

AMERICAN DYESTUFF REPORTER

LOUIS A. OLNEY
Directing Editor

NORMAN A. JOHNSON
Managing Editor

DEVOTED TO THE INTERESTS OF TEXTILE CHEMISTRY
• BLEACHING • DYEING • FINISHING • PRINTING •
AND THE NECESSARY MECHANICAL EQUIPMENT

"Circulated Everywhere Textiles Are Processed"

Subscription Price: $5.00 per year; Canadian, $6.80; Foreign, $6.00. Fifty cents per copy

VOLUME 25 | JUNE 29, 1936 | NUMBER 13

CONTENTS OF THIS ISSUE

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

General

The Wetting Power of Steam Distilled Pine Oils... 341
By E. V. Romaine and I. E. Knapp

Where Science Helps 346
By W. A. Lucas

Technical Notes from Foreign Sources..... 358

New Products; Trade Notes..... 364

Open Forum 367

Proceedings of
American Association of Textile Chemists and Colorists

The Manufacture and Properties of Acetate Yarn... P350
By V. L. Bohnson

Meeting, New York Section..... P356

Applicants for Membership..... P356

Editorial:

Chemical Production and Sales..... 357

Official Publication of the American Association of Textile Chemists and Colorists

THE OBJECTS OF THIS ASSOCIATION ARE:

"To promote increase of knowledge of the application of dyes and chemicals in the Textile Industry.

"To encourage in any practicable ways research work on chemical processes and materials of importance to the Textile Industry.

"To establish for the members channels by which the interchange of professional knowledge among them may be increased."

Published Every Other Monday

HOWES PUBLISHING CO. ~ ~ 440 FOURTH AVE. ~ ~ NEW YORK

CLOSING DATE FOR ADVERTISING COPY . . . . . MONDAY PRECEDING ISSUANCE DATE

NATIONAL

AVIROL

AH EXTRA

Its outstanding wetting-out and penetrating properties have received world-wide recognition never accorded to imitations • The only wetting-out agent and penetrant that is effective at all temperatures met in textile processing.

Kier Boiling *Degumming*

Warp Sizing *Dyeing*

Finishing

Its marked dispersing properties make it invaluable, particularly where hard water is encountered • For particulars and samples write our nearest branch.

NATIONAL ANILINE & CHEMICAL COMPANY, INC.

40 RECTOR STREET NEW YORK, N. Y.

BOSTON	150 Causeway St.	CHARLOTTE	201-203 W. First St.
PROVIDENCE	15 Westminster St.	GREENSBORO	Jefferson Standard Bldg.
CHICAGO	357 W. Erie St.	ATLANTA	140 Peachtree St.
PHILADELPHIA	200-204 S. Front St.	CHATTANOOGA	James Bldg.
SAN FRANCISCO	517 Howard St.	PORTLAND, ORE.	646 N. Thompson St.
	TORONTO 137-145 Wellington St., West		

Branches and Distributors throughout the World

NATIONAL QUALITY

NATIONAL QUALITY

AMERICAN
DYESTUFF REPORTER

VOLUME 25 JUNE 29, 1936 NUMBER 13

The Wetting Power of

Steam Distilled Pine Oils

By E. V. ROMAINE* and I. E. KNAPP†

THE use of steam distilled pine oils in the textile industry is becoming more widespread and hence there is increasing interest in their properties and behavior. The purpose of this paper is to describe certain studies that we have made of some of the factors which affect the wetting power of pine oil emulsions.

Steam-distilled pine oils are obtained from old pine stumps and "light wood" by the steam-and-solvent process, as described by Palmer[1]. For many years there was essentially only one grade of steam-distilled pine oil on the market, but now several different grades are available. The largest producers have their own special brands for these various grades which differ considerably from one another in their analyses and properties.

From a strictly chemical point of view pine oils consist of complex mixtures of terpenes, including tertiary alcohols (chiefly alpha terpineol), secondary alcohols such as borneol and fenchyl alcohol, and terpene hydrocarbons such as dipentene, terpinene, and terpinolene. By far the most important single constituent is alpha terpineol, that is, 1-methyl-4-isopropyl— Δ^1 —cyclohexen-8-ol. This tertiary alcohol constitutes from 50 to 80 per cent of commercial pine oils.

The three representative pine oils used in this investigation showed the following approximate analyses:

TABLE I

	Tertiary Alcohols	*Secondary Alcohols*	*Hydrocarbons*
GNS No. 5 Yellow...	63	14	10
Newport Heavy White	73	17	0
Newport Texil	83	12	0

Wherever pine oil is used in the textile industry, so far as we know, it is always in the form of an emulsion. In this respect it is similar to many other oils which are themselves insoluble in water but which can be emulsified by means of some emulsifying agent such as a soap or a sulfonated oil.

We do not know of any well-established, definite relationship between the chemical composition of an oil and its behavior in emulsions. However, Speakman and Chamberlain state[2] that "emulsification of an oil . . . is conditioned mainly by the magnitude of the oil-water interfacial tension"; in other words, the lower the interfacial tension the better the emulsification. It is a well-known fact that the presence of a polar group lowers the interfacial tension. For example, a pure hydrocarbon like n-octane has an interfacial tension against water of 50.8 dynes per centimeter, whereas n-octyl alcohol shows only 8.5[3]. It might be expected, therefore, that a pine oil containing no hydrocarbons and a high percentage of tertiary alcohols would show a relatively low interfacial tension; and if so, it should be easily emulsified.

In order to test this theory we have determined the interfacial tension of the representative pine oils mentioned in Table I, together with that of pure alpha terpineol and alpha pinene, a terpene hydrocarbon. The apparatus and procedure were similar to that described by Dimmig[4]. A carefully ground capillary tip on the short end of a glass tube bent like a J was immersed in water, and a measured volume of oil was allowed to flow through very slowly. On the basis of the number of drops that were formed from a definite volume of oil it was possible to calculate the interfacial tension of the pine oil against water. This calculation was made by means of the Tate formula as modified by Harkins and Brown[5]. This modified formula is used in the International Critical Tables, but the oiginal Tate formula is also used frequently (see, for example, Snell[6]). The experimental data obtained in our laboratory were therefore calculated by both formulae, as shown in Table II.

*Director of Technical Division, General Naval Stores Co., New York.
†Research Chemist, Newport Industries, Inc., Pensacola, Fla.

TABLE II

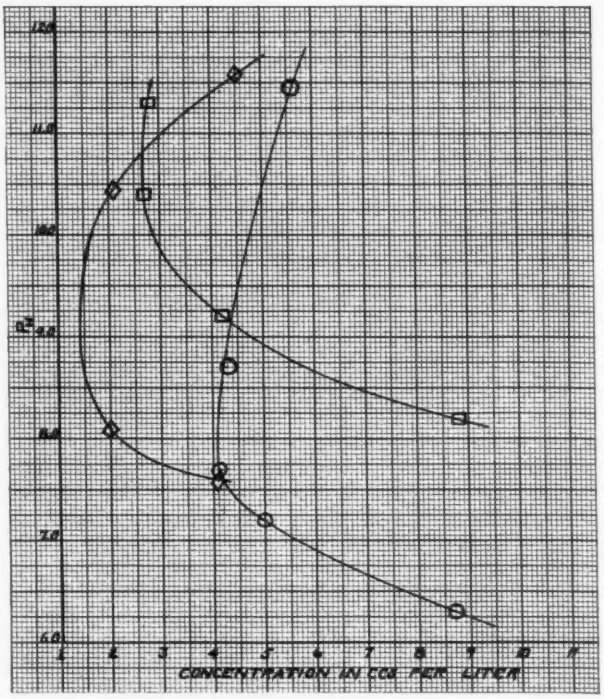
	Interfacial Tension Against Water (dynes per centimeter)	
	Harkins Formula	*Tate Formula*
Newport Alpha Pinene.....	39.0	34.4
GNS No. 5 Yellow.....	13.4	11.4
Newport Heavy White.....	12.0	10.2
Newport Texil	11.3	9.7
Alpha Terpineol.....	10.7	9.1

These results show that the greater the tertiary alcohol content of a pine oil the lower is its interfacial tension against water. The fact that a pine oil such as Newport Texil oil showed a low interfacial tension against water indicated but did not prove that its emulsions would show good wetting power for textile fibers. There are so many variables in the composition, preparation, and behavior of emulsions that it is not safe to make many generalizations without experimental evidence to back them up. We have, therefore, made a large number of tests to determine the relative wetting power of various pine oil emulsions, using different pine oils and different emulsifying agents, and with varying degrees of alkalinity.

The procedure used was that described by Draves and Clarkson[7] in a paper read before the 1930 annual meeting of the American Association of Textile Chemists and Colorists. Essentially this method measures the time required for a 5 gram skein of 2-ply unbleached cotton yarn to sink in the emulsion which is being tested, when the skein carries a 1.5 gram sinker and is held under the surface of the emulsion by an anchor. The wetting time was determined at two or more concentrations of wetting agent by taking the mean time for at least four skeins at each concentration. Ordinarily the concentrations were so chosen that one average time was between 15 and 25 seconds and another between 25 and 35 seconds. These times were plotted against the corresponding concentrations on log-log paper, and a straight line was drawn through the two points. The concentration which would give a wetting time of 25 seconds was then read off. This particular wetting time is an arbitrary figure but it was recommended by Draves and Clarkson and we have found it very satisfactory as a basis for comparison.

A rather wide variety of emulsifying agents was used in this study. "Concentrates" were prepared by mixing 20 parts of emulsifying agent with 80 parts of pine oil, and then a definite volume of this "concentrate" was emulsified in one liter of water at a temperature of 38-40° C. (100-104° F.). Ordinary Pensacola tap water having a pH of 6.2-6.4 was used in practically all these tests with the exception of a few tests with distilled water.

It was found that the pH of the emulsion had a very marked effect on the wetting time. The pH was determined with the LaMotte color standards and comparator. Since practically all the emulsions were very milky, the precision of this method was probably not greater than



Emulsifying Agents
⊙ - Sulfonated Castor Oil
◈ - Potassium Linseed Soap
⊡ - Product A

Fig. 1.

±0.2 pH. The hydrogen ion concentration in the emulsions was varied by adding small quantities of dilute acetic acid, or dilute solutions of sodium carbonate or sodium hydroxide.

The data obtained are shown in Table III. The "concentration" in the last column is the number of cubic centimeters of concentrate per liter which gave a wetting time of 25 seconds. With this information a number of interesting comparisons can be made. These can be shown most clearly by plotting the data in the form of curves, as shown in Figures 1-5.

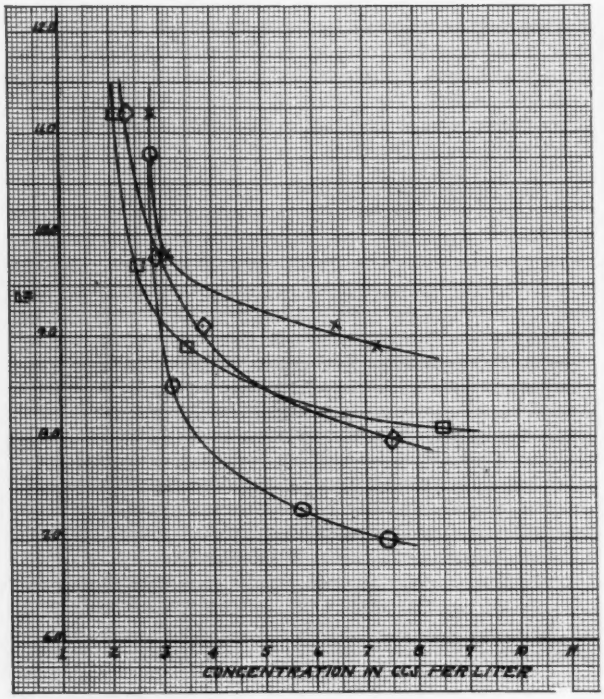
Figure 1 shows the results with three different emulsifying agents. No pine oil was present. Apparently each base behaves in its own characteristic manner and no generalization can be made.

The results obtained with the same pine oil (Texil oil) and different bases are shown in Figure 2. It is evident that these curves show a convergence in the vicinity of a pH of 10. The spread from maximum to minimum is roughly five times as great at a pH of 9 as it is at a pH of 10. These curves indicate that pine oil emulsions with these particular bases reach almost their maximum wetting rate at a pH of 9.8-10. Increasing the alkalinity still further causes only a very slight change. Each base seems to have a sort of critical range in which it is very sensitive to any change in the pH. For example, sodium

TABLE III

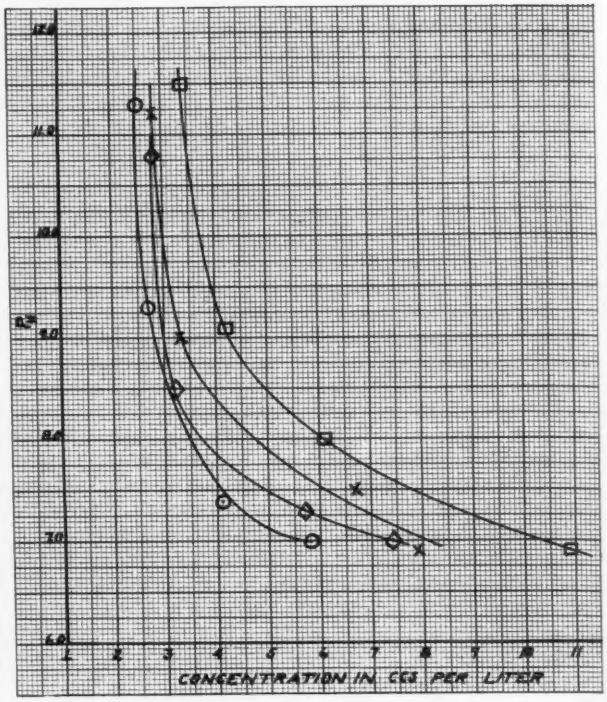
Emulsifying Agent	*Pine Oil*	*pH*	*Concentration for 25 seconds wetting time (cc.s per liter)*
Sulfonated Castor Oil	——	6.3 (a)	8.7
Sulfonated Castor Oil	——	7.2	5.0
Sulfonated Castor Oil	——	7.7	4.1
Sulfonated Castor Oil	——	8.7	4.3
Sulfonated Castor Oil	——	11.4	5.6
Sulfonated Castor Oil	Alpha Terpineol	7.0 (a)	5.8
Sulfonated Castor Oil	Alpha Terpineol	7.4	4.1
Sulfonated Castor Oil	Alpha Terpineol	9.3	2.7
Sulfonated Castor Oil	Alpha Terpineol	11.3	2.5
Sulfonated Castor Oil	Texil Oil	7.0 (a)	7.4
Sulfonated Castor Oil	Texil Oil	7.3	5.7
Sulfonated Castor Oil	Texil Oil	8.5	3.2
Sulfonated Castor Oil	Texil Oil	10.8	2.8
Sulfonated Castor Oil	Heavy White	6.9 (a)	7.9
Sulfonated Castor Oil	Heavy White	7.5	6.7
Sulfonated Castor Oil	Heavy White	9.0	3.3
Sulfonated Castor Oil	Heavy White	11.2	2.8
Sulfonated Castor Oil	No. 5 Yellow	6.9 (a)	10.9
Sulfonated Castor Oil	No. 5 Yellow	8.0	6.1
Sulfonated Castor Oil	No. 5 Yellow	9.1	4.2
Sulfonated Castor Oil	No. 5 Yellow	11.5	3.4
Product A	——	8.2 (a)	8.8
Product A	——	9.2	4.2
Product A	——	10.4	2.7
Product A	——	11.3	2.8
Product A	Alpha Terpineol	8.9 (a)	5.9
Product A	Alpha Terpineol	9.1	5.0
Product A	Alpha Terpineol	9.8	3.0
Product A	Alpha Terpineol	11.2	2.6
Product A	Texil Oil	8.9 (a)	7.2
Product A	Texil Oil	9.1	6.4
Product A	Texil Oil	9.8	3.1
Product A	Texil Oil	11.2	2.8
Product A	No. 5 Yellow	9.0 (a)	10.5
Product A	No. 5 Yellow	9.2	9.3
Product A	No. 5 Yellow	9.8	4.9
Product A	No. 5 Yellow	11.6	3.6
Potassium Linseed Soap	——	7.6	4.1
Potassium Linseed Soap	——	8.1 (a)	2.0
Potassium Linseed Soap	——	10.4	2.1
Potassium Linseed Soap	——	11.6	4.5
Potassium Linseed Soap	Texil Oil	8.0	7.5
Potassium Linseed Soap	Texil Oil	9.1	3.8
Potassium Linseed Soap	Texil Oil	9.8	2.9
Potassium Linseed Soap	Texil Oil	11.2	2.3
Sodium Oleate Soap	Texil Oil (b)	8.1	8.5
Sodium Oleate Soap	Texil Oil (b)	8.9 (a)	3.5
Sodium Oleate Soap	Texil Oil (b)	9.7	2.5
Sodium Oleate Soap	Texil Oil (b)	11.2	2.1
Product B	Texil Oil	7.9	9.4
Product B	Texil Oil	8.7 (a)	8.4
Product B	Texil Oil	10.8	4.0
Sulfonated Olive Oil	Texil Oil	6.4 (a)	6.0
Sulfonated Olive Oil	Texil Oil	8.4	4.9
Sulfonated Olive Oil	Texil Oil	10.8	3.4
Product C	Texil Oil	6.8	6.4
Product C	Texil Oil	8.6 (a)	6.3
Product C	Texil Oil	11.4	3.1

Product A was a well-known patented emulsfying agent, the composition of which was not known.
Product B was said to be a 50 per cent sulfonated castor oil.
Product C was a trade-marked emulsifying agent, the composition of which was not known.
Notes: (a) designates original emulsion without the addition of either acid or alkali.
(b) designates special concentrate made up with only 68 per cent pine oil; all other concentrates contained 80 per cent.



Newport Texil Oil with
⊙- Sulfonated Castor Oil
◈- Potassium Linseed Soap
×- Product A
⊡- Sodium Oleate Soap

Fig. 2.



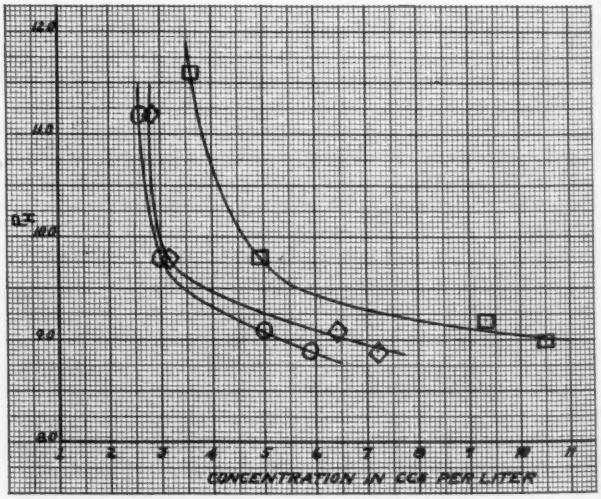
Sulfonated Castor Oil with
⊙- Alpha Terpineol
◈- Newport Texil Oil
×- Newport Heavy White
⊡- G. N. S. No. 5 Yellow

Fig. 3.

oleate soap with Texil oil required 8.5 cc. of concentrate per liter (for 25 seconds wetting time) at a pH of 8.1, but only 3.5 cc. at a pH of 8.9.

Figure 3 shows the effect of different grades of pine oil emulsified with the same base, i.e., sulfonated castor oil. Again the differences become much less as the alkalinity increases. However, the most interesting conclusion to be drawn from this family of curves is that the wetting power of a pine oil is a function of its tertiary alcohol content. At any given pH pure alpha terpineol shows the lowest concentration (for 25 seconds wetting time) followed by Texil oil, Heavy White, and No. 5 Yellow, in the order of their decreasing tertiary alcohol content (see Table I). Similar results were obtained when Product A was used as the emulsifying agent, as shown in Figure 4.

It was thought that possibly a direct comparison of the data for a base alone with that for the base plus pine oil might throw some light on the actual effect of the pine oil on wetting time. Figure 5 shows three such comparisons. It is obvious that a mixture of Newport Texil oil with Product A is practically as good as Product A alone under these conditions. A similar mixture with sulfonated castor oil is better than sulfonated castor oil alone at a pH of 8.0 and above. With the potassium linseed soap



Product A with
⊙- Alpha Terpineol
◈- Newport Texil Oil
⊡- G. N. S. No. 5 Yellow

Fig. 4.

the curves are so irregular that no conclusion can safely be drawn.

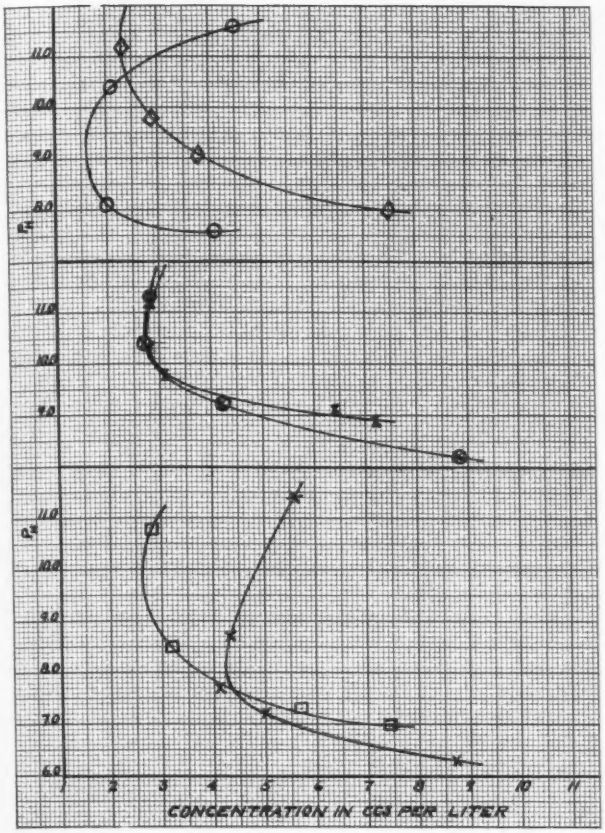

CONCENTRATION IN GMS PER LITER
⊙- Potassium Linseed Soap
Q- Potassium Linseed Soap with Newport Texil Oil
⊗- Product A
⧗- Product A with Newport Texil Oil
X- Sulfonated Castor Oil
⊡- Sulfonated Castor Oil with Newport Texil Oil

Fig. 5.

It has already been noted that most of these pine oil emulsions were very milky and it was, therefore, difficult to determine their pH by color comparison. We thought that perhaps this difficulty could be overcome by determining the pH of a solution of the base itself at the equivalent concentration. Since pine oil is neutral it ought not to interfere. It was found, however, as shown in Table IV, that in nearly every case the pH of the pine oil emulsion was distinctly higher than the pH of a solution of the base. This effect may possibly be explained as follows: the base hydrolyzes to some extent in water solution and the hydrolyzed acid portion may partially dissolve in the minute droplets of pine oil, leaving an excess of OH ions and thus producing a higher pH.

TABLE IV

	pH of Solution 2.0 gms. base per liter	*pH of Emulsion (2.0 gms. base + 8.0 gms. pine oil) per liter*
Sulfonated Castor Oil..	6.2	6.6
Product A	8.4	9.2
Potass. Linseed Soap..	8.4	9.3
Sodium Oleate Soap...	8.8	9.3
Product B	7.0	8.7
Sulfonated Olive Oil...	6.0	6.2
Product C.....	7.5	8.6

In conclusion, our studies have shown that the greater the tertiary alcohol content of a pine oil the lower is its interfacial tension against water and the faster it will wet cotton when it is emulsified. In other words when different grades of pine oil were emulsified with the same base it was found that the pine oil containing the highest percentage of tertiary alcohols required the lowest concentration for a given wetting time, with other pine oils following in the order of their decreasing tertiary alcohol content. This relationship held true at any pH, although the differences between high-tertiary and low-tertiary pine oils were smaller at the higher alkalinities (pH of 10 and above).

It has also been shown that when comparative data are to be obtained on the wetting rates of pine oil emulsions, it is of the utmost importance that the pH of the emulsions be controlled very carefully. In general the concentration required for a given wetting time varies inversely with the pH of the emulsion. This variation is not, however, a straight-line function for apparently the rate of change is much less in the more strongly alkaline solutions (pH of 10 and above). The difference in the concentrations required for a given wetting time between two pine oils emulsified with the same base, or between two bases with the same pine oil, is apparently greater at a pH of 9.0 or lower than it is at a pH of 10.0 or higher. We have found such wide variations in the behavior of the emulsifying agents which we have used that we do not feel we should recommend a definite pH at which all kinds of pine oil emulsions should be tested. What *is* important is that all comparative tests be made at the same pH.

Literature Cited

[1]Palmer, J. Ind. & Eng. Chem. *26,* 703 (1934).
[2]Speakman and Chamberlain, Technical Aspects of Emulsions, p. 107 (A. Harvey, London, 1935).
[3]International Critical Tables, IV, 437 (McGraw-Hill Book Co., 1928).
[4]Dimmig, Proc. A.S.T.M. *23,* 363-369 (1923).
[5]Harkins and Brown, J. Am. Chem. Soc. *41,* 499 (1919).
[6]Snell, J. Ind. Eng. Chem. *24,* 1053 (1932).
[7]Draves and Clarkson, Amer. Dyestuff Reptr. *20,* 201 (March 30, 1931).

Where Science Helps*

By W. A. LUCAS†

A SCOTCH cleric once said "Free and fair discussion will ever be found the firmest friend to truth."

In an organization such as ours, whose main reason for existence is the discussion and dissemination of knowledge, there is one essential requirement which we as an association must recognize, i.e., a spirit of tolerance and consideration of the opinions of its members. Our industry, and when I refer to that, I mean the wet processing of textiles, is one which has developed or grown out of the past through experience and practical experimentation. Today the industry operates largely on the results of those years of successes and failures. Had we reached the climax of perfection we would not be organized with the object of furthering scientific knowledge for the future development of our industry.

Let us review for a moment the objects outlined under our constitution. They are briefly:

1. "To promote increase of knowledge of the application of dyes and chemicals."
2. "To increase practical research of chemical processes and materials of interest thereto."
3. "To establish channels for the interchange of professional knowledge among its members."

These are very commendable objectives. By these words this organization has discarded the old dogmas of the past and consented to review any and all agencies which tend to improve the lot of the wet processor. This gesture bodes well for the future of our industry. Object number three of our association refers to establishing channels for the interchange of professional knowledge among its members. There is nothing more constructive to the development of our industry than the fullest application of this idea, on the successful fulfillment of which lies our future.

If, however, we limit our activity to meetings and conventions of the association we are losing sight of the most potent agency through which the dissemination of knowledge is possible, i.e., the individual members. It is hoped that the question box recently instituted may be instrumental in opening this avenue of thought.

PROBLEMS FOR RESEARCH

You will agree that the wet processing industry is a very fertile ground for research and development work. There is not an active member at this meeting, I venture to say, who could not, were he asked, present us with a problem for consideration. With the ever-changing demands of the trade, new problems arise every day. With these our members have to cope. It is in this respect that this association can be of greatest value to its members.

Our membership includes a diversity of dyers and chemists. While in a general way we may be doing the same thing, nevertheless, the variety of application renders our outlook and opinions slightly at variance with one another. It will be necessary, therefore, to coordinate as closely as possible all groups in discussion.

THE COMMON GROUND OF CHEMISTRY

Dyers and chemists meet on the common ground of Chemistry. The dye vat, the scouring dolly, the fulling machine, all performing a chemical duty.

Sir Francis Bacon, the great English philosopher, describes chemistry in these words:

"Alchemy may be compared to the man who told his sons of gold buried somewhere in the vineyard, where they by digging found no gold; but by turning up the mould about the roots of the vine, procured a plentiful vintage." To the search and endeavors, to make gold, have brought many useful inventions and instructive experiments to light.

One of the hardest things to learn is to outgrow our early beliefs. There is much in our industry which needs outgrowing. But due to the lack of more exact data we are obliged to continue our rule of thumb methods. This by the way exists not only in our own branch of the industry but also in others.

It is unreasonable to expect that the practical man, whose duties and problems absorb all of his time is to be burdened with the responsibility of creating and discovering new methods and applications for the improvement of processing. This is purely a function of the laboratory. It seems rather surprising under these circumstances that the industry in Canada does not take more advantage of the assistance which chemistry is able to offer.

SCIENCE AND PRACTICE

In the comparatively brief length of time that science has been associated with the textile industry, it has justified its connection. As remarked before, all wet processing is a function of chemistry. Today science and practice go hand in hand. If we were to list the benefits that science has brought to the industry, we would realize that it has become a living, fundamental necessity. The problems of our industry are still legion. But today, due to

*Paper read at the regular monthly meeting of the Ontario Section, Canadian Association of Textile Colourists and Chemists held at the Ontario Research Foundation, Toronto, May 2, 1936.

†Chief Chemist, Toronto Carpet Manufacturing Co., Ltd., and Barrymore Cloth Co., Ltd.

research of the past, we know what is happening in the dye-bath, the kier, the scouring bath, the printing vat, etc. Science has interpreted customary practices into controlled processes.

Let us consider the functions and duties of the laboratory in a mill organization. In a paper read before Committee D-13 of the American Society for Testing Materials, in 1930, by Mr. R. H. Adams of Calloway Mills, La Grange, Georgia, he says—

"Before the establishment of the textile laboratory, practically all material was produced against specifications supplied either by the purchaser or developed solely and expensively for standard production through bitter experience. Specifications were generally limited, and still are, to performance factors. For instance, it was specified that the strength must be so much in one direction, and that the burst must be so much in either direction. Usually it was known for what job the material was designed. But without means for research and testing, it happened many times that in meeting the specifications, a great deal of costly work was done which ranked simply as a dead loss, before the proper manufacturing conditions were located through the rule of thumb method which most mills followed."

This paragraph describes very nicely the chief function of a laboratory. One of the greatest sources of leakage in any manufacturing establishment where large quantities of raw materials are used in a slip-shod policy of accepting shipments on the basis of verbal or written specifications without a proper check on the receipt of shipment.

CHECKING RAW MATERIALS AND SUPPLIES

In these days of close estimating and costing, it is virtually impossible to figure yields and production unless the fullest information is known of the materials entering into the goods being fabricated. A good example of this type of raw material is wools and fleeces. The great variation of condition and extraneous matter met with in this material is so diversified as to require constant checking. This is not only necessary from a money value standpoint but for the proper control and standardization of the finished goods. The checking of raw materials against specification and of the finished goods against standards is one of the routine duties of the laboratory, an activity which does not vary to any great extent. The control of processed material within the plant also is usually included.

Many instances can be given of the value of routine checking of raw material. About fifteen years ago, we decided to standardize our whole line of materials, including soaps, oils, dyestuffs, chemicals, finishing materials, starches, dextrines, etc. For about six months the laboratory was kept busy setting standards and making out claims for deficiencies. The claims gradually tapered off when the suppliers realized that their shipments must meet standards and specifications. As a result, we are today receiving uniform shipments which not only assures us of money value but also uniformity of processing.

TESTING NEW MATERIALS

Besides the checking of regular shipments, the number of samples of new materials offered continue to increase each year. There are a number of good new products on the market today which have more or less merit. You will understand that I am speaking from a woolen standpoint only. The majority however can be classed as patent medicines of the trade. Some supply firms have the idea that any kind of substitute should be given a trial and most of them have little or no idea how the material functions. Much time, money and material can be wasted by indiscriminately trying new materials offered by inexperienced manufacturers. Some of these materials are the simplest of preparations offered at a fairly profitable price to the maker.

In the field of legitimate processing materials, the dyestuff firms and the chemical suppliers have performed a great service to the industry. Granting that the results react to their balance sheet, they deserve the gratitude of the trade for some very good products. Many a headache has been cured by a few pounds of the product of these supply houses. Most of them have chemists on their staff who have had experience in the textile field and who understand some of the problems of the man in the mill.

MAKING PRACTICAL TESTS

Practical evaluation in the mill should succeed an analytical valuation in the laboratory providing the material merits a trial.

Much time and labor is saved by this means. In many cases, it is possible by a cursory examination to determine whether or not a product finds application in your particular case.

There is, in most cases, a very wide margin between two practical trials, i.e., the apparent results may be a long way from the real. In order that a fine line of division can be drawn, the analysis together with any other precision test which can be made, should accompany the results of the larger application. In this way, the accuracy of many a practical trial has been proven to be inaccurate as a positive means of differentiating between two materials.

It should be borne in mind by the chemist when coordinating with the practical man on a problem that he is not interested in bewildering scientific terms. He isn't concerned about colloids, dispersoids, chromophores, surface tension, hydrolysis, etc. These terms have to be translated into popular illustrations in order to be impressive.

Will Rogers once said "Nothing you can't spell will ever work." As an illustration, I recall several years ago discussing a question of size with our carpet superintendent. The question concerned a suitable size for sizing stuffer warps for carpet. We had compared a new product

with our standard material, and one of the tests was the viscosity of a given solution. He inquired what significance this test had on the question. We explained at some length that the test was a measure of the relative loss in efflux velocity in a given time. He listened intently until we were through and then with a look of exasperation he burst out: What has all this damned viscosity, velocity got to do with it? What I want to know is "What the hell is its 'stickification.'"

PRODUCTION CONTROL

The control and standardization of intermediate products such as yarns, and the supervision of the preparation of materials necessary to processing is another duty the laboratory is usually charged with.

The investigation of mill troubles is a subject which requires considerable attention, but is too extensive to consider at this time. We all have our collection of interesting data concerning the subject, and great value can be derived from open discussion on these problems.

MEETING CONSUMER DEMANDS

During the past ten years, we have had a condition develop in the industry which has increased tremendously the need for the utmost efficiency of every man in the business. Due to the economic conditions of the world, the consumers market has assumed an attitude of "make it cheap enough and I'll buy it." This has necessitated many changes in processing and has served to bring out the best in every organization.

The repercussions of such a development, however, has not only affected the fabricators but also the raw material market. We find many of our fool-proof raw materials passing into the discard and new ones appearing which, though they may not be so comfortably handled, nevertheless have been found to be equally efficacious. If this development carries on into the future, there will be a greater demand for research in the industry. In fact, it is a great necessity even now.

RESEARCH AND DIVIDENDS

Research is a term that has been grossly abused. It is used very glibly by many well-meaning people, as a sort of cover-all when referring to scientific pursuits. Industrialists use the term particularly easy. They refer to research of this, research of that. If they were asked for one per cent of the profits to finance research, there is no doubt that the term would disappear from their vocabulary. Research requires money, time, equipment and personnel. It make take weeks, months or years before the objective is reached but during the process much valuable information is uncovered. Most well supported and properly conducted researches pay huge dividends, as witness the steel and rubber industries. Unfortunately, when a research laboratory becomes available to an industry the flood of problems and inquiries forces it to evolve itself into an analytical routine laboratory, at the expense of pure research.

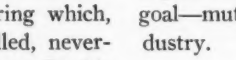
OPEN DISCUSSIONS WILL HELP

In my opinion, the greatest benefits are to be derived from discussions of problems submitted by members at our monthly meetings, and suggest that a fair length of time be included in the genda for these discussions.

I would also like to suggest that these discussions be taken verbatim for permanent record in the minutes. After a respectable period of time, it will be found that much useful information has been collected and we may see fit some time in the future to put these discussions in print. There is no doubt that a lot of latent talent and information is carried away from our meetings unspoken. We have men in the organization who have spent a lifetime in the industry and their fathers before them. In the past this knowledge has been handed down from father to son. Many of the ideas may have been outgrown but it is interesting to the younger members to see the evolution of our industry and many of the old formulaes make interesting reading and should be permanently recorded.

Here, I would suggest that some of our older members, dyers and finishers, resurrect some of those old formula books from the old trunk in the attic and present them to the meeting as a basis for the history of the evolution of wet processing, which idea I hope you will give some thought.

In closing, I want to record an appeal for the permanent and closest cooperation between the two types of members of our society—the practical man and the chemist. Let us differ in opinion. We may have to contradict tomorrow what we say today. If we never change our opinions, we never correct our mistakes. But never let us lose sight of the fact that we are all aiming at the one common goal—mutual assistance and the development of the industry.



Tris-azo Dyestuffs

German Patent No. 495,114 (*April* 3, 1930).—(*addition to G. P. No.* 467,060 *of September* 7, 1926).—*I. G. Farben-Ind. A.-G.*—The original patent covers the preparation of a black tris-azo dyestuff, formed by diazotizing p-amino-acetanilide, coupling with gamma acid in acid reaction, and diazotizing this amino-azo dyestuff and coupling to another molecule of gamma acid, this time in alkaline reaction; this dis-azo dyestuff being then diazotized and coupled to a molecule of m-phenylene diamine

The present additional specification covers the introduction of a further sulfonic group into the above product. The sulfonic group (previously introduced into one of the components, not by sulfonation of the finished product) may be contained in any one of the four components. The products dye cotton and viscose in deep black tones; acetate silk is not dyed by them, and if the weave is a mixture containing both cotton and acetate silk, the acetate element comes out a pure white.

One example is given.

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists
JUNE 29, 1936

Officers of the Association

WILLIAM H. CADY, *President*
U. S. Finishing Co., Providence, R. I.

A. R. THOMPSON, Jr.—ELMER C. BERTOLET, *Vice-Presidents*

WILLIAM R. MOORHOUSE, *Treasurer*
National Aniline & Chemical Co., Boston, Mass.

HAROLD C. CHAPIN, *Secretary*
Lowell Textile Institute, Lowell, Mass.

LOUIS A. OLNEY
President Emeritus and Chairman of the Research Committee
Lowell Textile Institute, Lowell, Mass.

Councilors-at-Large

JOSEPH F. X. HAROLD — HAROLD M. CHASE
DONALD H. POWERS — ARTHUR E. HIRST
CARL Z. DRAVES — HENRY F. HERRMANN

Councilors Representing Sections

BEN VERITY (Rhode Island) — R. M. RITTER (Philadelphia)
HANS MEYER (New York) — ELMER F. SMITH (Midwest)
ROLAND E. DERBY (N. New England) — R. S. WHEELER (South Central)
CHARLES B. ORDWAY (South Eastern) — CHARLES H. STONE (Piedmont)

Local Sections and Their Officers

Northern New England Section
Carl Z. Draves, Chairman, Ludlow Mfg. Associates, Ludlow, Mass.
John N. Dalton, Secretary, Pacific Mills, Worsted Division, Lawrence, Mass.

Rhode Island Section
John G. Masson, Chairman, Rosemont Mill, Woonsocket, R. I.
Raymond A. Pingree, Secretary, 7 Sayles Ave., Saylesville, R. I.

New York Section
George L. Baxter, Chairman, Bradford Dyeing Association, 40 Worth St., New York, N. Y.
P. J. Kennedy, Secretary, E. I. duPont de Nemours & Co., Inc. 61 Thomas St., New York, N. Y.

Philadelphia Section
Robert E. Sullivan, Chairman, Anchor Thread Co., Groveville, N. J.
R. W. Delaney, Secretary, National Aniline & Chemical Co., 200 S. Front St. Philadelphia, Pa.

Piedmont Section
Chester L. Eddy, Chairman, Renfrew Bleachery, Traveler's Rest, S. C.
Raphael E. Rupp, Secretary, Pacific Mills, Lyman, S. C.

South Central Section
Walter E. Hadley, Chairman, Standard Coosa Thatcher Co., Chattanooga, Tenn
Murray B. Smith, Secretary, Standard Coosa Thatcher Co., Chattanooga, Tenn.

Midwest Section
Arthur T. Brainerd, Chairman, Ciba Co., 325 W. Huron St., Chicago, Ill.
Elias A. Johnson, Secretary, National Aniline & Chemical Co., 357 W. Erie St., Chicago, Ill.

South-Eastern Section
C. A. Jones, Chairman, Georgia School of Technology, Atlanta, Ga.
Robert H. Harris, Secretary, Spalding Knitting Mills, Griffin, Ga.

Lowell Textile Institute Student Section
Herbert A. Wormwood, Chairman; Henry S. Anthony, Secretary

North Carolina State College Student Section
A. E. Shumate, Chairman; J. W. Furr, Secretary

Members should notify the **Secretary** immediately of all address changes

Standard Wash Fastness Samples

Cotton, Wool, Silk

The standard samples which have been in preparation for some time by the Sub-Committees on Fastness to Washing of Dyed Cotton and Dyed wool are now ready for distribution, and the original standard silk sample cards have been revised to correspond with the new system of classification first introduced in the 1934 Year Book.

These standards have all been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1934 Year Book and each set includes a dyeing representing each of the different classes of fastness.

With these sample dyeings for reference it will be possible to accurately grade the fastness to washing of any dyed cotton, wool, or silk fabrics, by comparing them with the standards after subjection to the standard washing tests as approved by the Association.

The A.A.T.C.C. is now prepared to furnish these three sets of washing standards for $3.00 or $1.00 per individual set which is to cover the cost of preparation.

All inquiries concerning these washing standards should be addressed to the Chairman of the Research Committee.

LOUIS A. OLNEY,
LOWELL TEXTILE INSTITUTE,
LOWELL, MASSACHUSETTS.

The Manufacture and Properties of Acetate Yarn*

By V. L. BOHNSON†

IT MUST be considered an honor to be invited to deliver a talk on the manufacture and properties of acetate rayon here in Boston, the birthplace of that yarn, for it was in Boston that about the beginning of the century Lustron, the first cellulose acetate yarn, was made. The infant industry, being a pioneer, was a little premature, because satisfactory conditions for its growth and survival had not yet come about; but today it is a very healthy child. There are today twenty-five plants in the world engaged in the manufacture of acetate yarn. Four of these plants are in the United States; three in France; four each in Italy, Germany and England; and one each in Belgium, Switzerland, Holland, Canada, Greece and Brazil. Another American plant is understood to have recently resumed operations.

The manufacture of this type of synthetic yarn has had a phenomenal growth in the United States. The year 1919 first saw the production here of the modern form of the yarn, 50,000 lbs. being manufactured; this was only 0.6 per cent of the total domestic rayon manufactured that year. In 1935, over 50,000,000 lbs. of acetate yarn was made—22 per cent of the total rayon production. The increase in production in the last year has been especially significant; whereas total rayon production in the United States increased from 208,000,000 lbs. to 256,000,000, or 23 per cent, the production of acetate yarn increased from 38,000,000 to over 55,000,000—an increase of 47 per cent.

This increase in the use of acetate yarn has been brought about not only because of the distinctive characteristics of this type of rayon, but also because of the current price trend which has been of such a short duration that it may not yet perhaps be entirely appreciated. As a result of research and increased production, costs have been so reduced that the average sales price of acetate yarn has decreased nearly 15 per cent over the past year, and in some deniers is now actually lower than the price of the corresponding viscose yarn. Acetate yarn still finds its greatest use in the weaving trade, which consumes about 86 per cent, whereas hosiery and other knit goods consume approximately 13 per cent.

As previously mentioned, this wide acceptance of acetate yarn, particularly in the weaving trade, is due to certain distinctive characteristics which it possesses as compared with the other types of artificial yarns. It is not—like the viscose, cuprammonium, and nitro-cellulose types of rayon—a regenerated cellulose, but is a distinctly different substance, an ester of cellulose, and consequently has distinctly different properties.

Before proceeding with a description of the procedure for the production of this novel type of rayon, it may be of interest to briefly review the origin and main features of its development. The technical literature on the subject is exceedingly voluminous and misleading, and consists mainly of patents. The industry is still in a highly competitive state, and a great many features of manufacturing processes are held to be trade secrets. The German cellulose chemist, Eichengruen, in his article on Acetylcellulose in Ullmann's Encyclopedia of Technical Chemistry, remarked that the manufacture of cellulose acetate was unique among chemical industries in that so much had been written about it and so very little technical progress actually made beyond the original discoveries. The substance—cellulose acetate—of which cellulose acetate yarn consists, has been known since 1865, when Schuetzenberger first prepared it by heating cellulose in a sealed tube at 180° C. with acetic anhydride. His product was not a useful article, being greatly degraded by the conditions of his experiment, and formed solutions of very low viscosity, yielding brittle films. About 15 years later Franchimont showed that a more interesting material could be made by treating the cellulose with acetic anhydride in the presence of such a catalytic material as sulfuric acid or zinc chloride. It was not until 20 years later, however, that any real technical advance was made. About 1900 a number of patents were issued to the German chemist Lederer and to the Bayer Company, which outlined the several procedures of manufacture of cellulose acetate very much as they exist today. In the interim Cross and Bevan, the inventors of viscose, had in 1894 attempted to make cellulose acetate and spin it into yarn but the venture was not industrially successful.

It was about 1900 also, as mentioned earlier, that the Lustron Company actually made yarn commercially by spinning the type of cellulose acetate then known from a solution in chloroform into an oil bath. Up to this time the substance as prepared by the various investigators was not soluble in ordinary cheap solvents such as acetone,

*Presented at meeting, Northern New England Section, April 3, 1936.

†du Pont Rayon Co.

being the triacetate of cellulose. A very pronounced advance was made in 1905 when it was shown by Miles that this ester could be partially hydrolyzed with water and that the resulting secondary product was soluble in a much larger variety of solvents than the cellulose triacetate from which it was prepared. The Bayer Company had actually begun commercial manufacture and in 1910 were selling cellulose acetate principally for film manufacture. At about this time also the Eastman Kodak Company and the Agfa organization in Germany were manufacturing cellulose acetate in a small way for use in safety (slow burning) film. In France the Usines du Rhone were similarly engaged, and legislation was actually contemplated looking toward the replacement of the more inflammable nitrocellulose film.

Such was the status at the outbreak of the World War. Commercial development up to this time, as we have noted, had been rather slow. War requirements for cellulose acetate, for use particularly in the doping of airplane wings, greatly stimulated its technical advance. The brothers Dreyfus, of Basel, Switzerland, who had been investigating the substance, entered the field and established plants at Spondon in England, and later in the United States.

At the close of the war, therefore, cellulose acetate existed as a commercial material, but specific war requirements no longer existed. It was fairly obvious, perhaps, that such a film and filament-forming material should be considered for spinning into a synthetic fiber in much the same manner as was already being done with nitrocellulose. Both the Dreyfus interests and the Usines du Rhone undertook such development work, and the investigations resulted in the commercial appearance of "Celanese" yarn in England, and of "Rhodiaceta" yarn in France. Because of the immunity of the new type of fiber to the existing types of dyestuffs, there were at first pronounced obstacles to its success, but they were satisfactorily overcome. Development was then rapid, with the growth which has been previously mentioned.

The essential technical steps in the manufacture of cellulose acetate yarn are few and simple. The cellulose is first esterified with acetic anhydride to produce cellulose acetate of the desired characteristics; this acetate is then dissolved in a suitable solvent to yield a heavy viscous solution, and this solution is forced through minute orifices to form filaments which solidify upon evaporation of the solvent. Subsequent operations are largely mechanical and are similar to those in use with other textile fibers. This field of manufacture, therefore, may, for the purpose of description, be divided into two parts: (1) the manufacture of the cellulose acetate; and (2) the manufacture of the rayon.

There are two important essential materials in the manufacture of cellulose acetate:

A. Purified cotton linters.

B. Acetic anhydride.

While glacial acetic acid is used in the process, it may be considered primarily a by-product. The cellulose used must be of high quality; experience has shown that the preparation of cellulose acetate is one of the severest requirements which a chemical cellulose is called upon to meet. There have been many published statements to the effect that wood pulp can be used for the manufacture of cellulose acetate and, owing to the possibility of lower and more stable prices, there is much activity in its investigation, but so far in actual commercial practice properly selected and purified cotton cellulose has been used. Selected second cut linters are purified by kier boiling with dilute sodium hydroxide for several hours to dissolve soluble cellulose and non-cellulosic constituents and are then bleached with chlorine or hypo-chlorites, washed, dried, and baled. Careful control over these processes is very necessary in order that the quality of product shall be satisfactory and uniform, and thus contribute to a satisfactory and uniform cellulose acetate.

The other essential material, acetic anhydride, is the most expensive ingredient in the manufacture of cellulose acetate. Attempts have been made to cause the cheaper glacial acetic acid to react with cellulose, but they have not been successful, and the more active acetic anhydride must be used. (A similar reaction takes place with acetyl chloride, but is not commercially used). Prior to the growth of the acetate industry the production of acetic anhydride was relatively small; the needs of the acetate industry have stimulated the development of processes for its manufacture. There are a number of such processes, among which we may briefly mention the production from sodium acetate by heating it with sulfur chloride or sulfur and chlorine in the presence of acetic anhydride itself as a medium; this is the classic manufacturing process. Among newer processes are the dehydration of acetic acid by passing its vapor over heated dehydrating catalysts, and the production from acetylene by the manufacture and subsequent decomposition of ethylidene diacetate. The acetic acid necessary for manufacture by the sodium acetate or the dehydrating process may be obtained, as you know, either by the distillation of wood, the oxidation of alcohol, or by oxidation of acetaldehyde synthetically prepared from acetylene.

In the preparation of cellulose acetate, the two essential materials react with each other according to the following equation, which is very similar to that which can be written for the esterification of a simple alcohol.

$$\underset{162}{C_6H_7O_2(OH)_3} + 3\,\underset{306}{(CH_3CO)_2O} \longrightarrow 3\,CH_3COOH + \underset{288}{C_6H_7O_2(CH_3COO)_3}$$

However, the reaction is complicated by the physical and colloidal condition of the cellulose and of the cellulose

acetate formed. It is accompanied by the degradation or hydrolysis of the cellulose to a smaller molecular size and by the dispersion of the soluble cellulose acetate formed in the acetic acid present. The reaction mass is at first heterogeneous and is of high viscosity, has a low heat conductivity and requires special means of agitation in order to obtain a uniform product. It is necessary to use certain catalysts to accelerate the reaction, and it is a wide practice to specially pretreat the cellulose for the acetylation. Such materials as formic acid, acetic acid, alkalis, oxidizing agents, sulfuric acid and lactic acid, have been suggested as agents for such pretreatment. Whereas the common catalyst is C.P. sulfuric acid, a large number of other materials has been suggested and patented for the purpose; such as zinc chloride, perchloric acid and perchlorates, mixtures of phosphoric acid and sulfuric acid, acid sulfates, phosphorus and sulfur chlorides, sulfonic acids, and so on ad infinitum.

Although there has been in the past some interest in a procedure of acetylation by which the cellulose acetate formed does not go into solution that is, remains in the original fibrous form of the cotton), it is customary in present day manufacturing to conduct the reaction in the presence of a solvent such as acetic acid. Obviously, the more acid used, the more mobile and easily agitated is the viscous liquid with consequent improvement in reaction conditions; on the other hand, all this acid is subsequently diluted and must be recovered. The actual amount used will, therefore, vary widely in practice and depend upon an economic balance between the factors involved. One very interesting modification of the acetylation reaction is that in which liquid sulfur dioxide is used as the solvent; this process has enjoyed some commercial success.

Practice varies widely as to the equipment used for the acetylation reaction, although it must be of such a type as to permit agitation of the viscous mass and control of the temperature of the reaction. In some plants large closed cylinders rotating upon a horizontal axis are used; special types of such mixing equipment have been tried. In other plants, a modified form of dough mixer with special agitators is used.

The properly blended cotton linters are charged to the mixing device, together with the acetic anhydride and the desired quantity of acetic acid for use as a medium; the necessary amount of catalyst, carefully weighed, is also added. The acetylator is then closed and agitation begun. The reaction being exothermic, the temperature rises and is controlled by external cooling with brine or cold water. If the temperature is allowed to get too high the hydrolysis of the cellulose molecule becomes predominant, whereas it is desired to suppress this side reaction in order to preserve a satisfactorily high viscosity in the ultimate product. The reaction is followed by observing the disappearance of the cellulose fibers by examining the viscous dope in the microscope. When the fibers have disappeared the reaction is complete and must be stopped to prevent further degradation. The product, in solution, is cellulose triacetate or primary cellulose acetate, having the following general formula. All of the hydroxyl groups of the original cellulose have been esterified, and in their place we find 3 CH_3COO groups.

$$[C_6 H_7 O_2 (OH)_{3-n} \quad . \quad (CH_3 COO)_n]_x$$
$$[C_6 H_7 O_2 (CH_3 COO)_3]_x \text{ where } n = 3$$

It can be precipitated at this time by dilution with water, and washed but, as previously pointed out, it is unsuitable for commercial use because of its limited solubility and the fact that it is impervious to water and in the form of yarn is difficult to dye and finish.

In order, therefore, that this primary intermediate product may be converted to a substance having utility, it is not separated from solution but is hydrolyzed to an acetone-soluble form by the action of water. Water in the form of dilute acetic acid is added to the viscous mass which is then transferred from the acetylating vessel to a tank where it is allowed to stand for a period of time at a controlled temperature. The water reacts with a part of the acetyl groups of the cellulose triacetate with the liberation of acetic acid. Samples are taken from time to time and tested by precipitation of the dissolved material and examination for composition and solubility. When the hydrolysis has proceeded to the desired point, the entire mass is precipitated.

Conditions for hydrolysis vary widely in practice from, for example, several days at room temperature to a few hours at 40 to 60°. At the present time, practically all acetate yarns are made from cellulose acetate of the same average composition, approximately 39 per cent acetyl. The secondary cellulose acetates are acetone soluble in the range between 37 per cent and 40 per cent acetyl. As the latter increases, the moisture resistance of the product increases, but the depth of dyeing of the resulting yarn decreases. General solubility characteristics also vary with change in composition. The commonly used value is regarded as the best compromise from all points of view, and slight differences in yarns made by different producers are in part due to slight differences in the particular average value used.

When the hydrolysis to secondary acetate has proceeded as far as desired, reaction is stopped and the material precipitated in one of a number of different ways. Among methods which have been described are: Spraying into dry hot air, addition of such a non-solvent as toluene with agitation, extruding and shearing off the shreds resulting from evaporation of the acetic acid, the addition of ethylene chloride and subsequent precipitation in a hot bath, and so on. Precipitation must be carefully controlled to obtain a satisfactory easily soluble form of product and a not too dilute acetic acid. The simplest method is to run the gum into water with vigorous agitation in such proportions that the supernatant liquid is below the

concentration in acetic acid which will soften the acetate. This supernatant liquid is drawn off and sent to acid recovery, while the finely divided chalky-white flaky precipitate is transferred to a large washing vat and washed with very carefully purified water until it is neutral and free from uncombined acid. It is then extracted in a centrifugal or in squeeze-rolls, and dried in some convenient type of dryer. The product is then ready for transfer to storage bins, where it is held until required for the spinning operation, or for other commercial uses.

As thus prepared the cellulose acetate is a white amorphous flaky solid of low apparent density but of a specific gravity of 1.33. It is not a simple chemical compound but it is a mixture of highly polymerized complex substances of which the following may be written as the general formula:

$$[C_6 H_7 O_2 (OH)_{3-n} \cdot (CH_3 COO)_n]_x$$

It can be separated into simpler constituents by fractional extraction or precipitation and it has no sharp melting point but softens at about 240° C. It has a low affinity for moisture; is stable toward heat and toward ultra-violet light; has a high insulating capacity; and is soluble in acetone or mixtures of acetone and alcohol, from which it can be deposited as a tough transparent flexible film by evaporation of the solvents. The two characterizing properties of the acetate are its viscosity, which may vary over a wide range depending upon conditions of its manufacture, and its composition as represented by the per cent acetyl radical which it contains. Both the composition and the viscosity must be carefully controlled in order to produce batches of uniform behavior.

Because of its properties, cellulose acetate has a number of other commercial uses in addition to its employment in the manufacture of yarn. Among them may be briefly mentioned its use in the interliners of safety glass, its use in plastic molded articles, in safety photographic film, and in "Cel-O-Glass"—the material so widely used for greenhouses and poultry houses. In safety glass and molded articles its plastic characteristics are of importance; in safety film its slow burning characteristics; and in "Cel-O-Glass" its power to transmit ultra-violet light.

It has been mentioned that the dilute acetic acid drawn off the precipitated cellulose acetate is sent to a recovery operation. It will have been noted that, in addition to the constant quantity of acetic acid which is used as a medium for the reaction, there is also a certain quantity of acetic acid produced by the reaction between the anhydride and the cellulose and by the hydrolysis of the primary acetate. This whole amount of acetic acid which is relatively quite large is now present as a dilute material, and must be reconverted to glacial acid in order that the constant quantity may be re-employed in another acetylation operation. It would obviously be economically impossible to waste all or any of this acid. The excess resulting from the reaction can be converted to acetic anhydride for further use. There are a number of methods of acetic acid recovery, which may more properly be called acetic acid concentration. It is impracticable to directly distill such a dilute solution. It is, therefore, either usually extracted with a solvent which dissolves the acetic acid from the water, such as isopropyl ether, cresol, ethyl ether, or certain hydrocarbons, from which the extracted acid is then separated; or the water may be removed from the dilute acid by azeotropic distillation with an entraining agent such as normal propyl acetate which, upon distillation, carries off the water leaving practically glacial acid behind. This glacial acid may then be converted to anhydride by one of the processes previously noted. It is a practice in some plants to convert the dilute acetic acid by means of soda ash to sodium acetate, which can then be converted to acetic anhydride.

This is a convenient point to note that the acetate process for the manufacture of yarn is one in which all the essential materials are recovered, even the waste. In this matter it has a distinct advantage over its competitors among synthetic yarns.

The cellulose acetate having been made and stored until such time as it is required for use, we are now ready to proceed with the preparation of the spinning solution for the manufacture of acetate yarn. A solution is required of such concentration and viscosity that it can be forced through fine holes into a coagulating medium. The solvents most generally used are either acetone or mixtures of acetone and alcohol, and the concentration of the solution varies in practice from 18 to 25 per cent, depending upon the viscosity of the cellulose acetate used. The mixing operation takes place in closed mixers, equipped with heavy stirrers because of the high viscosity of the dope and requires from 12 to 24 hours to completely disperse the cellulose acetate in the solvents. Very careful control is maintained over the concentration, composition and viscosity of the solution. Before charging the acetate a number of lots are blended in order that the contents of the various mixer lots may be as uniform as possible. When solution is complete the charge is transferred by pumping it to a blending tank which holds several batches, and where further blending takes place, still further insuring uniformity. It is filtered several times under high pressure through thick cotton filters, in order to remove incompletely dissolved materials, and is then stored to remove dissolved air bubbles before it is transferred to the feed tanks for the spinning machines.

As you know, it is common practice to manufacture the so-called dull or delustered yarns by the incorporation of certain pigments, such as titanium oxide, in the yarn. Such a material is added and dispersed in the mixing operation; the amount added is very carefully controlled and the luster of the yarn is dependent upon the amount used. A wide variation in luster is, therefore, possible

between bright yarn on the one hand to a very chalky yarn on the other. I have seen one foreign plant where five types of dull yarn were in production.

Since the viscose and cuprammonium processes involve wet spinning (that is, spinning of the solution into a solvent which would coagulate the yarn) it was natural that the wet spinning of cellulose acetate solution should receive attention. A good many patents have been issued on the subject for such operations as the spinning from solutions in various solvents into coagulating baths of ether, water, carbon tetrachloride, benzine, naphtha, and so on. The general process, however, has never had any practical success and is probably fundamentally too slow in operation and too complicated by the need for further purification, to warrant consideration unless some specially desirable property may thus be obtained. The dry spinning operation, on the other hand, which originated with nitrocellulose yarn, is characterized by a simplicity which permits effective control of the physical and chemical characteristics of the yarn and insures better quality, since there is less danger of tangling filaments. Since the chemical composition of the yarn is the same as that of the material from which it is spun, the manufacturing process is complete at the spinning machine except for the mechanical operation of twisting and packaging the yarn. No purification process, with its attendant troubles and hazards to quality, is necessary.

In principle, the dry spinning operation consists simply in extruding the viscous spinning solution through fine holes in a spinneret into a current of warm air which evaporates and carries off the solvent, thus solidifying the filaments. Various methods of carrying out this operation are in vogue, although in principle they are essentially the same. A spinning machine may consist of from 25 to 100 spinning positions. Each one of these positions consists of a spinning pump, either of the multiple piston or gear type, which is a precise metering device for delivering solution to the nozzle; a spinneret nozzle, which is a round jet of nickel or other non-corrodible metal perforated with the desired number of holes of .002 to .005" diameter; a tube or box (generally known as the "spinning cell") through which warm air flows for the evaporation of the solvent; and a winding device at the other end of the cell. Among the variations in the process are: current and countercurrent air flow; air entering at both ends of the cell and leaving at the center; extrusion upward through the cell; extrusion downward through the cell; and so on. It is probable that results are not greatly different, no matter what the particular procedure for evaporation, provided that very careful control is maintained over solution temperature, air temperature, air velocity, and air humidity. These conditions are so adjusted that the yarn leaving the cell is free from solvent. I believe that there have been processes in use, in which the solvent is simply condensed by chilling a portion of the spinning cell, but they are not very efficient as to solvent recovery and the characteristics of the yarn are somewhat more difficult to control.

Obviously, the number of filaments in the thread is determined by the number of holes in the spinning nozzle. The size of these holes is in part dependent upon the fineness of filament desired but for the most part the filament denier is determined by the relation between the rate of delivery of spinning solution and the windup speed. As the filaments leave the cell they are drawn together and led to some form of winding device, which may consist of a rotating bobbin or spool, a cap or ring-twisting spindle, or a spinning bucket.

At this point the yarn is practically finished except for twisting and winding into packages. Very careful chemical control has been maintained over every step of the process, both in the manufacture of cellulose acetate, in the preparation of the spinning solution and over the conditions of spinning, in order to maintain as uniform a product as it is possible to make.

The acetone or acetone-alcohol vapors mixed with air which are drawn from the spinning cells are conducted to a recovery system, the type of which depends upon the solvent used. They may, for example, be absorbed by activated carbon which is then steamed out and the condensate distilled to recover the solvent, or they may be passed through a tower in which the solvents are scrubbed out of the air with water and the water solution subjected to distillation. This recovery procedure, like that for acetic acid, is necessary for the economic success of the operation.

The yarn coming from the spinning operation is ready for twisting. If it has been collected on cap spindles it may already have a small amount of twist which is increased on the twister to the amount desired. Cellulose acetate yarn being a newcomer in the rayon field, it has been able to take advantage of the newer and more improved types of textile machinery. The earlier rayon yarns adopted the silk machinery then in use. Since that time twisters, reels, and spooling machines have been more heavily and sturdily built; cams and traverse mechanisms have been improved; lubrication systems have been designed to protect the yarn from contamination; and the equipment has been made suitable for operation at increased production speeds and with larger packages. Some recent improvements have been made in tensioning equipment and in spindle-driving mechanism on cone winding and copping machines. Both up-twisters and down-twisters are in use in various plants.

Suitable air conditions for textile operations are 70° F. and 60 to 65 per cent relative humidity; under these conditions acetate yarns process most satisfactorily. In the winding operations, in which the yarn is drawn off "over-end" from the twister packages, very careful attention is given to the inspection of guides, and adjustment of ten-

sions in order that the yarn may not be stretched beyond the permissible limit. The density of packages is also kept under control. During these operations also the filament count, denier, twist, moisture content, tenacity and elongation, dye absorption, and visual appearance of the yarn are frequently and periodically checked in order to maintain control upon the operation. It is customary, during the textile operation, to apply to the yarn a finish for the purpose of lubricating the yarn, binding the filaments together and eliminating static. This finish is tinted with fugitive dyestuffs in the case of certain yarns such as, for example, those which are to be used in men's hosiery.

The distinctive properties which characterize cellulose acetate yarn and which differentiate it from other synthetic yarns are broadly traceable to its chemical and physical characteristics. It will therefore be of interest to briefly summarize these characteristics, and point out their specific influences.

Chemically, as already noted, the substance material of the yarn is an ester. To the composition of this ester is due the solubility of the yarn in such solvents as acetone, glacial acetic acid, formic acid, ethyl acetate, hot alcohol-water, hot alcohol-benzol, chloroform-alcohol, ethylene chloride, phenol and pyridine. By the use of these solvents it can be distinguished from regenerated cellulose rayon. On the other hand, it is not soluble for example, in dilute cold acid, cold benzol, naphtha, carbon disulfide, carbon tetrachloride, gasoline, ether or methanol. The fact of its solubility in certain solvents somewhat limits the activities of the dry cleaner, although at the present time the dry cleaning industry is sufficiently aware of its properties so that very rarely is any trouble encountered.

Because it is an ester, also, it does not dye in the same manner nor with the same types of dyestuffs as do other fibers, but does dye with a special class of dyestuffs which it is capable of dissolving. It will, in fact, take up dry dyestuffs if allowed to remain in prolonged contact with them.

The fact that it dyes with a special class of dyestuffs and could thus be cross-dyed formed the original basis of acceptance by the trade. Although this is still of importance, particularly in men's hosiery, the brilliance of color in acetate dress fabrics in plain shades is well known. Because of the nature of acetate dyeing, and the uniform composition of the product, acetate fabrics dye more evenly than those made from other yarns. (It is obvious, of course, that yarns from one manufacturer may dye slightly differently than those from another).

Although certain acid colors may be used as fugitive tints for acetate yarn, it will, in the presence of solvent or water, dissolve the colors in such a way that they cannot be readily discharged. Tinted acetate yarn should, therefore, not be allowed to remain wet for any length of time before scouring. In general, it is immune under proper conditions to the effect of other classes of dyestuffs. With these matters you are much more familiar than I am.

Also because it is an ester, it can be hydrolyzed by acids or alkalis, the extent depending upon the conditions involved. It should therefore be scoured with care, avoiding the use of too strongly alkaline liquids, as superficial saponification will result in uneven dyeing, staining with direct dyestuffs, and weakening of the yarn. Mild alkalis such as very dilute ammonia have relatively little effect.

Cellulose acetate has a lower moisture regain than cellulose under the same conditions. This may be predicted from the lower number of hydroxyl groups in the molecule. At 25° C. and 60 per cent R.H. acetate yarn has a regain of 5.2 per cent, whereas that of viscose yarn is 12.2 per cent; the commercial or shipping regain values are 6.5 per cent and 11 per cent respectively. The lower affinity for moisture thus indicated determines a number of the characteristics of the yarn. It is less sensitive than regenerated cellulose yarns to such fluctuations of relative humidity as take place, for example, between winter and summer. It is best handled at a regain of 6.5 per cent, or at a relative humidity of 60 to 65 per cent. When wet, the yarn maintains its original diameter and length to a greater extent than do other yarns. It is immune to body stains and perspiration; water spots do not often occur on acetate fabrics; it dries quickly after washing; pleating is retained under conditions of high moisture; it is more resistant to mold growth than are other yarns; sizes do not readily penetrate the yarn and are more easily removed.

On the other hand, this lack of affinity for water necessitates more care in wetting out acetate fabrics before dyeing.

Because of the difference in shrinkage between acetate and viscose yarns, the two are used in combination fabrics with interesting results, such as in matelasse crepes. It can be shown that crepes with a much better pebble are obtainable when acetate yarn is used in the warp. Because of this same characteristic, acetate yarns are finding important outlets in bathing suits for women and in linings for men's suits.

Cellulose acetate yarn softens at a relatively low point—around 200 to 240° C. While in one way this is a disadvantage, since it requires care in pressing with a hot iron, it has become an advantage in such special uses as the manufacture of stiffened collars.

Acetate yarn has a density of about 1.33 as compared with 1.5 for regenerated cellulose yarn, 1.25 to 1.3 for silk, and 1.32 for wool. This lower density, together with the smooth surface resulting from the dry spinning process, may explain the distinctive hand and drape which sets acetate fabrics apart from those made from other yarns.

The tenacity of acetate yarn is somewhat different than that of viscose yarn. At 70° F. and 60 per cent R.H. it is approximately 1.4 gms. per denier when dry and 0.9

gm. per denier when wet, whereas viscose yarn has approximately the same wet strength but a dry strength of 1.8 gms. per denier. Thus viscose yarn when wet loses 50 per cent of its strength while the acetate loses only about 30 per cent. This higher relative wet tenacity is again a function of the relatively lower affinity for water.

The dry elongation of viscose yarn at the breaking point is approximately 23 per cent, while that of acetate is about 26 per cent; when the yarns are wet, the elongations are 30 per cent and 37 per cent respectively. At high humidities acetate yarn stretches less with a given load than does viscose yarn, but it is considered that 0.5 grams per denier is the maximum permissible tension which should be applied to acetate at 60-65 per cent relative humidity. It has been shown, moreover, that acetate yarn is less susceptible to the effect of differences in dyeing than is a regenerated cellulose yarn.

One or two more items may be mentioned. Acetate satins are superior in drape and in resistance to creasing; acetate transparent velvets are unsurpassed in appearance, but unfortunately when crushed the pile is difficult to restore to its original appearance. It is to be hoped that the newer anti-crease procedures may be of some assistance in overcoming this.

In knit goods, the elastic recovery of an acetate fabric, after stretching, approaches that of silk, being superior to that of fabrics from other rayons.

With these distinctive effects obtainable, it is not strange that acetate yarn has won a prominent place among textile fibers.

In closing, it seems fitting to point out that the manufacture of a high quality rayon like cellulose acetate and, particularly, Du Pont "Acele" is not only a technical problem but an operating problem, and that a satisfactory product depends fully as much upon the many individual operators as upon the technical staff or technical process. The Du Pont Company attempts, through training, supervision, and cooperation, to bring home to every employee the customer's viewpoint; the reasons for high quality; the effects of defects. A regular and continuous compaign is maintained to the end that we may turn out as uniform and as perfect a yarn as possible.

MEETING, NEW YORK SECTION

THE last regular monthly meeting of the New York Section was held on Friday evening, May 22nd, 1936, at the Chemists' Club, New York City, at 8:00 P.M.

Richard Feibelmann, Technical Director, Aktivin Corporation, presented a paper entitled: "Hydrosulfite and Vat". Henry F. Herrmann, Chairman of the Sectional Nominating Committee, submitted the following names:

George Baxter, Chairman; Louis S. Zisman, Vice-Chairman; P. J. Kennedy, Secretary; John J. Sokolinski, Treasurer.

Sectional Committee—Mr. Ephraim Freedman, Mr. Robert H. Gaede, Dr. Jos. F. X. Harold, Dr. Harold De Witt Smith.

Councilor—Dr. Hans Meyer.

Member of National Nominating Committee—Dr. Harold De Witt Smith.

The candidates were elected unanimously.

George Baxter, the newly elected Chairman, expressed his appreciation to the Section, both for himself and his fellow-officers, for the honor of representing the New York Section during the coming year.

Also at this meeting, Henry F. Herrmann, Chairman of the Outing Committee, outlined an excellent program for the Annual Outing to be held at the North Jersey Country Club, Paterson, N. J., on June 26th.

There was a total attendance of approximately fifty-five (55).

Respectfully submitted,

P. J. KENNEDY, *Secretary.*

APPLICANTS FOR MEMBERSHIP

Active

John A. Barrington—Salesman, General Dyestuff Corp., New York, N. Y. Sponsors: J. R. Bonnar, W. L. Swenson.

Norman T. High—Foreman, Spring City Bleach & Dye Works, Spring City, Pa. Sponsor: A. E. Jones, Jr.

Ernest C. Kontz, Jr.—Textile Research Chemist, Tubize Chatillon Corp., Rome, Ga. Sponsors: R. H. Harris, H. W. Field.

George W. Sharpe—Asst. Colorist, Rock Hill Printing & Finishing Co., Rock Hill, S. C. Sponsors: Nathan Webber, R. S. MacDougall.

Henry D. Sharpe—Asst. Colorist, Rock Hill Printing & Finishing Co., Rock Hill, S. C. Sponsors: Nathan Webber, R. S. McDougall.

Junior

Luther M. Adams—Dyehouse Office, Rock Hill Printing & Finishing Co., Rock Hill, S. C. Sponsors: Nathan Webber, J. W. McCalla.

Joseph E. Jones—Laboratory Assistant, Rock Hill Printing & Finishing Co., Rock Hill, S. C. Sponsors: Nathan Webber, J. W. McCalla.

James Leon Moore—Technical Demonstrator, E. I. du Pont de Nemours & Co., Inc., R. & H. Chemicals Dept., Charlotte, N. C. Sponsor: R. M. Levy.

AMERICAN
DYESTUFF
REPORTER

LOUIS A. OLNEY, Sc.D.
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor
A. P. HOWES, Publisher
NORMAN A. JOHNSON
Managing Editor
MYRON DREW REESER
Advertising Manager
Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

Subscription price: $5.00 per year; Canadian $6.80; foreign $6.00

Vol. 25 June 29, 1936 No. 13

CHEMICAL PRODUCTION AND SALES
Comparative Figures

ALTHOUGH figures in themselves are generally uninteresting except to statistically-minded persons, when these figures deal with a particular industry or branch of an industry they become of interest to the persons who are directly or indirectly connected with that industry. Thus we believe you will find of interest certain preliminary figures which were recently released by the United States Tariff Commission concerning the production and sales of dyes and other synthetic organic chemicals in the United States during 1935. These figures show large increases in output of practically all groups of products.

Many unusual increases in production are noted among the synthetic organic chemicals which are not of coal tar origin. The total output of this group was 1,591,000,000 pounds with sales of 790,995,000 pounds, valued at $86,053,000 representing an increase over the preceding year of 40 per cent in production, 24 per cent in sales poundage and 18 per cent in sales value. Among the more spectacular increases in production are listed the following: synthetic methanol, 41 per cent; acetic anhydride, 73 per cent; acetic acid, 50 per cent; acetone, 70 per cent; amyl alcohol, 100 per cent; isopropyl alcohol, 90 per cent; fermentation citric acid, 50 per cent. Chemicals used in the automobile and motor fuel industries, synthetic fiber industry and solvents used in the dry cleaning industry also showed substantial increases.

Seventeen per cent greater production of dyes in 1935 over 1934 was recorded, indicating an output of 101,817,000 pounds during last year. This figure was 9 per cent less than the peak year of 1929. However it is explained that if the output of indigo in 1929 and 1935 be deducted from the totals for the respective years, the 1935 production would exceed that of 1929 by 6,000,000 pounds or 7 per cent. The production of indigo has shown a sharp decline in recent years from 29,320,000 pounds in 1929 to 13,614,000 pounds in 1935.

New dyes and unclassified dyes accounted for a portion of the increase. The total production of such dyes in 1935 amounted to 11,586,000 pounds, 20 per cent more than in the previous year. Acetate silk dyestuffs showed a particularly large increase as indicated by a 65 per cent greater production, 44 per cent increase in sales volume and 87 per cent increase in sales value, all figures compared with the previous year.

Dyestuff sales for all groups were 16 per cent greater in 1935 by poundage and 19 per cent greater value than during 1934. The unit value of sales for 1935 averaged 53c per pound against 51c in 1934.

The chemical industry also registered a gain during 1935 in the production of intermediates, total production being 436,811,000 pounds, sales totaling 191,055,000 pounds which were valued at $26,114,000. This production exceeded 1934 by 12 per cent and 1929 by 24 per cent. It is noted that in making the comparison with 1934 a certain adjustment of the figures was necessary due to the fact that in 1934 rubber chemicals were classified as intermediates, whereas in 1935 they were included in miscellaneous finished coal tar products. Other groups of chemicals which shared in the increased production were synthetic resins, resins from tar acids, coal tar medicinals, photographic chemicals, chemicals for rubber, diazo salts, rapidogene colors, synthetic tans and textile assistants.

The table shown below indicates very clearly the trend in sales and production of dyes and other synthetic or-

Comparison of United States Production and Sales of Dyes and Other Synthetic Organic Chemicals 1925-30, 1934, and 1935

Coal-tar chemicals	1925-30 *average*	1934	1935	*Increase 1935 over 1934*
	Thousands of pounds			*Percent*
Intermediates:				
Production	267,492	388,872	436,811	12.3
Sales	109,133	161,845	191,055	18.0
Sales value	22,408	21,914	26,114	19.2
Finished coal-tar products:[1]				
Production	138,078[2]	205,838[2]	270,835	31.6
Sales	133,964[2]	180,451[2]	228,798	26.8
Sales value	65,027[2]	81,333[2]	98,087	20.6
Dyes—				
Production	94,003	87,178	101,817	16.8
Sales	92,207	84,309	97,826	16.0
Sales value	39,428	43,251	51,405	18.9
Medicinals—				
Production	4,508	10,024	10,023	....
Sales	4,106	8,224	8,950	8.8
Sales value	7,464	7,921	8,372	5.7
Flavors and perfume materials—				
Production	3,966	4,168	4,364	4.7
Sales	3,919	3,695	4,080	10.4
Sales value	2,901	3,028	3,171	4.7
Coal-tar resins (1927-30)—				
Production	24,442[2]	56,059[2]	89,473	59.6
Sales	22,135[2]	43,351[2]	64,641	49.1
Sales value	7,756[2]	10,127[2]	12,191	20.4
Synthetic non-coal-tar chemicals				
Production	379,972	1,133,719	1,591,106	40.3
Sales	264,006	639,410	790,995	23.7
Sales value	44,499	72,878	86,053	18.1

[1] Includes color lakes, photographic chemicals and miscellaneous coal-tar products not shown separately.
[2] Does not include coumarone and indene resins.

ganic chemicals. While the readers of this journal have a particular interest in those dyes and chemicals which are used in the wet processing branch of the textile industry the trend for these products is indicated in a general way by the figures here quoted. These figures show a healthy condition of the chemical industry and in many cases of the related industries which must use chemicals in large quantities.

Technical Notes from Foreign Sources

"Micelle-Starches"

Monats. f. Textil. Ind. 48, 176 (1933).—There are, in general, two "kinds," really forms, of starches in use at present in textile work; the ordinary, or true, starches, which with hot water yield thick pastes, and the so-called soluble starches, that is, starches of the first sort which have been so altered in nature (really chemically degraded or broken down) that they are soluble in hot water, and no longer possess the ability to form pastes, as the term is ordinarily and definitely used; that is, they are really no longer true starches. Each is used in textile work for its own definite purpose, and there is no question of either one being desired to serve for the purpose of the other.

The effect of each kind, in imparting some particuiar property to the goods for which it is employed, is definite; but with the true starches, e. g., potato and corn starches, the paste produced is often really quite too thick and too viscose at the same time, to be suitable for use where this type of starch is the one really required. A 10% paste of potato starch is so viscous that, even at 75° C., it will not pass through the capillary of the viscosimeter, while under the same conditions the same amount of water will run through in 15 seconds. Thus, the relative viscosity of the paste and of water would be, at, say, 70° C., more than as 240/1. Naturally, such pastes, which will hardly pass through the capillary of the viscosimeter, of 0.5 to 1 mm. in diameter, prevents them from penetrating into the interstices of yarn and weave, and producing the effect desired. It is, therefore, often necessary to resort to means of diminishing the viscosity of such pastes, without alteration of the other desirable properties, though this is not always possible to bring about. There are in general three methods employed:

(a) by chemical breaking down of the true starch (that is, really, breaking it down to simpler, semi-starches). The thick paste is treated with small amounts of some substance which will "open up" the starch particles, which it is plain does really involve some degradation, at least, of the starch molecule, and a corresponding depression of the viscosity of the paste. The resultant less viscous and thinner paste may be suitable for certain purposes, but for other uses such a paste would no longer be of much use. It is also difficult, even if possible, to halt the process of breaking down the starch at exactly the point at which the desired properties reach their maximum, without the process going further and too far.

(b) by compromising. A thick paste of the true starch is diluted with a solution of soluble starch. This is a mere case of dilution; the viscosity of the mixture depends upon the viscosity of the thicker, true starch, which is hardly influenced by the much lower viscosity of the soluble starch solution. Again, then, while such a mixture may, and in some cases does, possess the properties desired, in other cases the residual evil properties of the true starch prevent the use of the mixture for particular uses.

(c) by mechanical modification. When a thick starch paste is subjected to vigorous mechanical agitation, the physical properties of the starch molecule are altered, and apparently the molecular structure is either altered to smaller dimensions, or the larger entities are broken up into micelles, or at least smaller groups of micelles (we are not able as yet to say positively which). At all events, by "beating", or by repeated violent agitation by pumping for some time, the thick paste becomes considerably thinner. It is known that no chemical, but only a physical "stepping down" of the starch particles is thus brought about, and though, because of clumsy machinery and loss of time involved, the method is only a device for gaining its effect, not a genuine and definite method, yet it seems to be a genuine advance in conception of the problem.

A number of products are now being marketed, under different names, in general following the title of "Micelle Starches", which have been prepared mechanically in some way parallel to that just mentioned, and in a definite way. Pastes from such products become thinly fluid by short warming; there is essentially no chemical alteration of the starch involved. The paste at first, say a paste of 10%, is very viscous; when warmed for only a few minutes, it becomes thinner, of excellent viscosity, and of very good penetrating power. After about 10-15 minutes warming, the maximum of change has been reached, and further warming produces no alteration in properties. In such preparations, the clearness of the paste is increased, and also the elasticity of the film; and goods treated with it are of a full consistency or body, and yet are not stiff.

Dyestuffs for Cellulose Esters and Ethers

German Patent No. 495,620 (*April* 9, 1930).—*I. G. Farben-Ind. A.-G.*—This group of products covers the mono-azo dyestuffs obtained by coupling various diazo

salts of the dinitro-amino-phenols, or their derivatives, to unsulfonated or uncarboxylated amino-naphthols, in the presence of neutralizing agents.

For example, 2-4-6-trinitro-3-methyl-phenol (trinitrated m-cresol) is partially reduced, as by sodium or ammonium sulfide, and the product, a mixture of 4-6-dinitro-2-amino-3-methyl-phenol and 2-4-dinitro-6-amino-3-methyl-phenol, is diazotized as usual for aminophenols, and coupled to 1-amino-7-naphthol, in the presence of sodium acetate, to neutralize the mineral acid set free, without introducing complications by use of carbonate or caustic with a nitrophenol. The product is sparingly soluble in cold water. It is dissolved in a suitable amount of water, and the goods dyed in a 1/20 bath-ratio, neutral, with 20 per cent of Glauber salt. This product dyes acetate silk a violet brown. The dyeing can obviously be diazotized upon the fiber and developed with beta-naphthol (giving a black) or with 2-4-toluylene-diamine (giving a bluish-black). All of the dyeings are of good fastness to water and washing especially, and of good fastness also toward agents.

These products are among the first which can be applied to the fiber in question directly, in neutral or slightly acid bath, to give blacks.

Amino-Azo-Sulfaminic Acids (Azo Dyestuffs)

German Patent No. 496,744 (*April* 10, 1930).—(*addition to German Patent* No. 409,524 *of April* 30, 1930). —*I. G. Farben-Ind. A.-G.*—The original patent, No. 409,564, protects the preparation of sulfaminic acids of azo dyestuffs, consisting in the coupling of any desired diazo-salt to the sulfaminic acid of alpha-naphthylamine. The present addition to the above procedure extends the process to cover the sulfaminic acids of alpha-naphthylamine-sulfonic acids and their derivatives. By employing the ordinary conditions in coupling (soda as alkali to neutralize the mineral acid set free, and maintaining a low temperature), the sulfaminic acid grouping is retained unaltered in the product—which will be a mono-azo dyestuff containing a sulfonic acid group or groups, and the sulfaminic acid group also, each as the alkali salt. The sulfonic acid group contained in the sulfaminic acid group is easily split out by warming with dilute mineral acid, so that the product, in substance or on the fiber, then contains a free amino-group, which makes it possible to diazotize and couple to a suitable component, or, on the fiber, to develop with such a component. If treated with nitrous acid as usual in diazotizing, the sulfaminic acid group is split, and the resulting amino-group diazotized, in one and the same reaction.

Vat Dyestuffs Containing Sulfur (Benzanthrone Series)

German Patent No. 497,737 (*May* 13, 1930).—*I. G. Farben-Ind A.-G.*—The fundamental substances of the procedure here protected are anthraquinonyl-mercapto-benzanthrones (except anthraquinonyl-Bz-1-mercapto-benzanthrones) or anthraquinonyl-mercapto-dibenzanthronyls, which are treated with alkaline condensing agents.

For example, 20 parts of caustic potash and 15 parts of absolute alcohol are heated together to solution, and at 160°-170° C. (the alcohol being by that time expelled, except for residual small amounts) are added 5 parts of 1′-anthraquinonyl-6-mercapto-benzanthrone. The mixture is kept at the above temperature until no more dyestuff is evidently being formed, then cooled, boiled up with water, and the boiling continued until the dyestuff, which at first dissolves as its leuco-derivative, has completely precipitated, when it is filtered off, washed, and dried. The blue-black powder thus obtained is purified by boiling out with any suitable high-boiling organic solvent, being practically insoluble in organic solvents even at the boiling-point. Its hydrosulfite vat is violet-red; the oxidized dyeings upon vegetable fibers are a greenish navy-blue, which do not redden when wetted with water.

The Analysis of a Sulforicinoleate

H. Tatu—*TIBA* 11, 403 (1933).—A thoughtful paper, partly descriptive and detailed, partly discussive—a view of the subject as a whole.

The author makes some general statements, by way of introduction, worthy of being recalled, though not new. As he remarks, the analysis of a sulfonated castor oil, and, in general, of any sulfonated natural oil, is not as simple a matter as one might think, for the sulfo-ricinate (as he calls it) of soda or ammonia is not a definite, homogeneous substance, in the chemical sense. To say that it is the product of the reaction of sulfuric acid upon castor oil is not a definition, for the products obtained in a single "reaction" of the sort are certainly different, according to the concentration of the acid, the temperature at which it reacts, and the duration of the reaction; it is evident that, even with the same percentage—content in sulfur, two sulfo-ricinates are not at all necessarily identical, their properties, even upon those lowest terms, depending upon the manner in which the sulfur is linked to the rest of the molecule.

This difference, also, is dependent upon the fact that the commercial products have been prepared for over forty years for a predetermined purpose, and, the purposes in view in the use of the product having altered during that period, we look today for certain qualities which no one formerly thought to ask for. In the earlier period, when dyeing with mordants was in favor (alizarine dyeing for Turkey red), dyers sought for sulfonated oils which would give a good Turkey red; nowadays, especially since the introduction of the Naphthol AS and similar dyestuffs, what one looks for first of all is an oil which is very soluble, very stable, insensitive to hard water, and possessing a vigorous penetrating power. The manufacture of the commercial product has been greatly modified in details, as a consequence, and the composition of the commercial products is rather different from what it formerly was.

The author states that the process of analysis is a particularly delicate one, and that older methods, formerly

held in favor, are of little significance; that other methods, formerly ignored or unknown, are of a very real importance now. He divides the paper, then, into four main topics; (a) the composition of castor oil, (b) its sulfonation, (c) the analysis for a normal sulfonated castor oil, and (d) the detection of adulterants. Of these topics, (a) does not offer much of interest, at least not new enough to be worth mention, and is brief. But the second topic, that of the process of sulfonation, is of very great interest, in view of its suggestions as to what really takes place in the apparently simple process of "sulfonation", a term to which the reviewer has before now objected, on the ground of its loose and uncertain application, as compared to its definite and fixed meaning in systematic organic chemistry.

The reaction of sulfuric acid upon a vegetable oil is a process much more complicated than would at first be supposed; the reactions of the mineral acid upon the constituent glycerides and the fatty acids derived from them, and forming their basis, are in number more than a few.

The "sulfonation" of a mono-ethylenic glyceride, such as oleic glyceride, is, to start with, very complex in nature, as a result of the secondary reactions of condensation and dehydration which may be involved; but this complexity of possibilities is naturally still greater in the case of ricinoleic glyceride, because of the reactions possible which involve the hydroxyl groups present. Thus, according to the (simplified) classification of Dr. Beyer (TIBA Nov. 1929 and subsequent issues), they may be noted thus:—

1—Saponification of the glycerides; this reaction, formerly questioned by some, is today generally admitted to take place. The glycerides are simply hydrolyzed by contact with the concentrated sulfuric acid, with liberation of their fatty acids (and of course their glycerol in addition). It is probable that this hydrolysis is progressive, and proceeds more energetically as the amount of water in the mixture increases, as a result of the formation of the sulfuric acid esters of the alcoholic groups; it proceeds more energetically as the working temperature increases. As a consequent conclusion, an oil "sulfonated" at a lower temperature contains a recognizable amount of unsaponified glycerides.

2—Formation of sulfuric esters. This reaction can take place with either the glycerides or the fatty acids derived from them by hydrolysis, and can take place either upon the OH group in the chain, or upon the double linkage in the chain—at least four possibilities, therefore, in the same mixture. In any case, the products, as touching the affected part of the molecule, are merely esters, still possessing a free-acid nature, (probably only one of the hydroxyls of the sulfuric acid react), and are none too stable against attack by reagents, being easily saponified (the sulfuric acid split off again, and the hydroxyl or double bond set free again—this might take place by the action merely of water under suitable conditions).

3—Saponification of these sulfuric esters. This reaction is the immediate result of the only slight stability of the groups; it takes place normally at once when the "sulfonation"-mixture is neutralized with ammonia or soda. It even takes place to some extent during the sulfonation, through the water liberated in the reaction. The result altogether is, that, if the cold sulfonation has produced a disulfuric ester, one molecule of acid reacting with the hydroxyl, and another with the double linkage in the chain, of the fatty acid, such an ester, upon saponification, will form a dihydroxy-compound, dihydroxy-stearic acid.

4—Formation of sulfonic acids (true). This reaction, to which too little attention is often paid, differs entirely from that of (2); *it results from the substitution of a hydrogen of a* CH_2 *group by the radical* SO_2OH, and takes place particularly when the concentration of the acid, and the temperature, are each high. Such a grouping is little liable to hydrolysis, except by rather violent chemical means (true sulfonic acids are almost always comparatively stable, when obtained in the "orthodox" manner—that is, by direct replacement of a hydrocarbon hydrogen by the sulfonic radical).

5—Reactions of condensation. The four types of reaction above mentioned are simple ones, dealing with single molecules at a time. But other reactions may also take place simultaneously; some, the result of two or more molecules of ricinoleic or of dihydroxy-stearic acid reacting with each other, the acid group of one forming an ester with the hydroxyl group or groups of another (or with the hydroxyls of the glycerides as yet unsaponified or partly saponified), and others, the result of the acid sulfuric esters of one or more, or the true sulfonic acids, or both, forming esters with the hydroxyl groups of other free acid or glyceride molecules. It is plainly evident how extremely numerous are the possibilities of such reactions. Such complications would ultimately lead to the formation of products almost impossible to be disentangled analytically, if the possibility of their being set up were not limited by working at a low temperature, and for a time not too long.

The different groups of substances possibly formed are quite different in type, and in the properties which they impart to the product. It is necessary to draw an essential distinction as to the sulfur content, between sulfuric acid involved as an ester and as a sulfonic acid. The author expresses himself as to this distinction as follows:

The sulfuric esters, he says, are the less interesting compounds, being unstable by nature, decomposed easily by alkalies, and even by dilute acids, with the formation of hydroxylated acids (ricinoleic and dihydroxy-stearic acids). It might be stated, without hesitation, that a sulforicinate which contains esters of this sort only would behave fundamentally as merely an alkali salt of, say, dihydroxy-stearic acid, since the greater part of the sulfuric acid would no longer be combined with the organic radical. In this case, an extreme supposition doubtless, but more frequently occurring than one would suppose, false conclusions would be drawn regarding the value of such a preparation, which would not at all deserve the

title of a sulforicinate; its wetting-out and emulsifying powers would be very low, and, in the presence of calcium salts, there would certainly occur a precipitation of the calcium salts of dihydroxy-stearic acid.

On the other hand, the sulfonic acids (true) are substances of much more interest; not being of ester nature, they are not saponifiable (at least, not by the ordinary means); they are quite resistant to the action of acids and alkalies, even in the heat; the sulfonic groups, attached directly to a carbon atom of the chain, can be removed only by vigorous treatment with (probably only fused) caustic alkali; their wetting-out power is considerable, their alkali salts do not hydrolyze in boiling solution to yield free caustic, as do many of the soaps, and, finally, the calcium and magnesium salts of all sulfonic acids being soluble in water, they do not precipitate in hard waters. It has also been found that the presence of such sulfonic acids in a mixture stabilizes, to some extent, the sulfuric acid esters which will probably also be present.

It is plain, then, that all the advantages are in favor of these true sulfonic acids, and that, in fact, the essential point in analysis is not the determination, in a commercial product, of the total combined sulfuric acid, but of the amount definitely fixed in the true sulfonic condition. This determination is a very delicate one, and it is probably because few consumers pay any attention to this point, that so many products which are sulfo-ricinates only in name are met with in commerce.

In any case, it is certain that true sulfonic acids form in an ordinary "sulfonation", along with the commoner sulfuric acid esters; it is, in fact, impossible so to conduct the preparation as to produce only one or the other type; but, by controlling the temperature and the concentration of the acid, by the various manipulative details so carefully kept secret, by the use of suitable catalysts or of special sulfonating agents, it is perfectly possible to increase or decrease the proportion of the true sulfonic acids, and so to modify the properties of the product obtained.

To recapitulate, then, and ignoring a certain number of secondary reactions which really complicate matters much further, we may find in a commercial sulfo-ricinate the following products:—

1—Castor oil unaltered, and the free ricinoleic acid resulting from its hydrolysis.

2—Mono- and disulfuric acid esters of the oil, or of the ricioleic acid derived from the hydrolysis of the oil, the acid function remaining in the molecule of these esters being neutralized by alkali.

3—Hydrolytic products of these esters, that is, the corresponding hydroxy-acids.

4—Sulfonic acids, in the form of their alkali salts.

5—The condensation-products of alcoholic acids inter se (polyricinoleic acids), and the sulfonation products of such complex acids.

6—Lastly, the inorganic sulfates resulting from the neutralization, by soda or ammonia, of the sulfuric acid incompletely removed by washing.

Certainly, even in this simplified summary, a complex mixture!

Descriptions and discussions of analytic methods follow. Of these, the determination of water, and of the percentage of ash, are briefly taken up, with some pertinent comments. The third topic, the determination of fatty matter, the author introduces with the remark that here the confusion begins, the manufacturers not being in accord as to what should be understood exactly by the term. To bring a little order into the confusion, the author proposes to distinguish between total fatty content and emulsified fatty content.

The determination of total fatty content may be carried out gravimetrically or volumetrically. The first method involves heating in the presence of dilute sulfuric acid with the addition of a known weight of high-melting paraffine, which, when melted, will act as an extractant for fatty matter set free; and, upon cooling, the solid cake of paraffine, washed, dried, and weighed, will by its increase in weight give the figure for the fatty matter yielded by a given weight of the oil. The second method, the volumetric, is less exact, and consists briefly in heating the sample with dilute sulfuric acid, in a long-necked flask carrying graduations upon a convenient part of the neck; after decomposition of the oil by the acid is complete, the contents of the flask are brought to such a volume, by addition of more dilute sulfuric acid or Glauber salt solution, that the separated oil, floating upon the surface, is brought within the graduated part of the neck of the flask, where its volume can be read off directly. The weight of the separated oil is calculated from its volume and the average specific gravity of a"normal" sulforicinate.

The author remarks (this section closing the first part of the paper) that neither of these methods is very exact, and that each rests upon a questionable basis; that any unattacked castor oil will be partly saponified, and its glycerol content lost in the aqueous part of the mixture; the sulfuric acid esters will be saponified, and their fatty content taken with the general fatty fraction; but the sulfonated components will not be hydrolyzed, and will remain in solution in the aqueous fraction, at least in part (even with use of Glauber salt in the second method). Thus, the analytical figures are both inaccurate, and do not give any general information as to the most interesting components of the product—the actually sulfonated portion.

—— ♦ ——

Polymethine Dyestuffs (Basic)

German Patent No. 499,967 (*June* 25, 1930).—*I. G. Farben-Ind. A.-G.* — 1-3-5-trialkyl-2-methylene-indolines or their salts are condensed with pyridinium compounds, in which the nitrogen is loosely attached, as, for example, in the di-nitorphenyl-pyridinium compounds and the pyridinium-cyanogen halides, or with the dyestuffs derived from such compounds by reaction with primary or second-

ary amines. For example, dinitrophenyl-pyridinium chloride (the addition product of dinitro-chlorbenzene and pyridine) is dissolved in pyridine with two mols. of 1-3-3-trimethyl-2-methylene-indoline, and the mixture warmed at 100° C. until the blue dyestuff no longer increases in quantity. The mixture is then poured into hot water, filtered from some resinous matter, and the dyestuff salted out. It dyes tannined cotton, silk, etc., a very clear, pure greenish-blue.

A structural formula is given for the product, but it is impossible to see how such a structure could originate from the components mentioned, without a large amount of faith.

Vat Dyestuffs

German Patent No. 495,732 (*April* 10, 1930).—*I. G. Farben-Ind. A.-G.*—In the procedure here protected, arylthioglycollic acids are condensed with o-diketones capable of so condensing, or with such o-diketones or their derivatives as are capable of so condensing in the presence of phosphorus pentoxide. In case the pentoxide is used, the oxythionaphthenes produced as intermediate steps react at once with the diketones, and are withdrawn from any possible further action of the pentoxide. It is best, when employing the pentoxide, to dilute it with some suitable inorganic inert solid, to prevent its aggregating into a mass; or else the reaction may be carried out in a medium which will withdraw the phosphoric acid formed from hindering the reaction.

For example, 1-chlornaphthalene-2-thioglycollic acid is mixed with isatine, and the mixture dissolved in technical dichlorbenzene. To the hot solution is added finely divided silica, and the mixture boiled for a short time. On cooling, the dyestuff is filtered off. The accompanying silica is removed by treatment of the impure product with caustic soda liquor.

Several examples are given; the colors are mostly of a bordeaux red type.

Action of Caustic Soda of Various Strengths Upon Wool

Dipl.-Ing. R. Jaeger-Monats. f. Textil-Ind. 49, 17 (1934).—The author briefly states, by way of introduction, "It is a well-known fact that mercerized cotton dyes in deeper tones than does common cotton; through printing of caustic soda pastes upon cotton weaves, and subsequent dyeing, a two-tone effect is attained. The same result is obtained upon woolen weaves, though not so strikingly as upon cotton. The question as to whether and how the wool substance is altered in the process, will be definitely taken up in what follows:"

The present, the first, section of the paper is as concise as the above introduction would promise. The author selected merino wool as the raw material, since this sort consists of pure wool fiber of a considerable uniformity. It was first cleansed in a Soxhlet with organic solvents, and then subjected to the action of caustic soda liquors of 2°, 9°, 16°, 24°, 27°, 35°, 41°, 46°, and 50° B. for periods of 2, 10, and 25 minutes, at room temperatures. The samples were inserted into test-tubes containing the different portions of caustic liquor of the different concentrations, and stirred about vigorously, to dislodge air-bubbles; at the end of the desired time-interval, they were withdrawn, thoroughly and vigorously washed, and dried in air.

At the concentrations of 16°, 20°, 24°, 27°, and 35° B., a decided swelling of the fiber was evident. The caustic liquor itself became yellow, and after 25 minutes immersion the wool appeared to have been converted to a yellow slime. While, after immersions of 2 and 10 minutes, the fibrous structure of the wool, after washing and drying, again became visible, the case was not thus after immersion for 25 minutes; the fibrous structure was entirely lost, and there remained a hard, brittle, wholly felted mass of substance, from which it was impossible to withdraw any individual fiber or hair. Even with two minutes immersion, it can be seen, with the eye alone, that felting takes place more and more rapidly as the concentration of the caustic increases; this felting reaches the maximum at a caustic concentration of 24°-27° B., the concentrations beyond that point affecting the aspect of the wool less and less, until, at 50° B., the aspect of the wool is hardly altered. The same holds good for reaction-intervals of 10 minutes; only, of course, the action of the caustic proceeds further; with a 25-minute immersion, the action is so violent that the fibrous structure is altogether lost. It is astonishing that concentrations of 16°-35° B. produce such profound alteration, while concentrations of 41°-50° B. do not bring such a change about.

The washing of the samples must be not only thorough, but even violently rapid, in manner, in order to remove as much of the caustic as possible in as short a time as possible, in order to diminish, as far as may be, the effect of the weaker caustic, produced by dilution of the stronger caustic in the material, with its consequent alteration of the effect already produced by the higher concentration, and so vitiating the results, as would be the effect of washing in the ordinary, deliberate way. The process must be not only that of washing out the caustic, but removing it, as far as humanly possible, immediately.

The general effect of such treatment is perfectly evident to the eye alone. The author, of course, proceeded further, testing the breaking-strength of the material after treatment, washing, and drying, the determinations being carried out upon single wool-hairs (average of 20 in each case). The average of uniformity was determined as 78 per cent.

A table of numerical results of the tests is given, and the figures are astonishing. With the concentrations above 40° B., the final breaking-strength of the fiber is greater after 25 minutes immersion than it is after a two-minute treatment. A 10-minute immersion in these high concentrations brings about a slight loss in breaking strength,

which rises within a total of 25 minutes to a higher value than that gotten from the 2-minute-immersion samples.

A graph is also included in this section of the paper.

—— • ——

Chemical Scouring in Textile Plants

A. Molner—Monats. f. Textil-Ind. 49, 64 (1934).—Attempts to remove the naturally occurring wool-fat from wool in a "chemical" way, by means of organic solvents, are of rather ancient date, so to speak. The most varied solvents have been proposed, and more than one form of suitable apparatus has been patented. But this method of scouring has never penetrated very deeply into actual technical use, whether because the solvents at first used were dangerously inflammable, or because the apparatus necessary was inconvenient. Certainly, at the present time, these difficulties have been overcome. The industry has at its disposal not merely non-inflammable, but incombustible, solvents, such as trichlor-ethylene, Asordine, etc. The apparatus now available is so constructed that a method of working absolutely beyond criticism is made possible. The method has also been so perfected that the degreasing can be carried out without damaging the wool to the slightest extent. Some textile plants practise the chemical method of scouring with satisfactory results; for example, scourers who deal with pitchy wool. It is plainly evident that the chemical method can show a series of advantages for a plant carrying on only ordinary, routine work—handsome aspect of the goods, only slight losses in washing, no bleeding of the colors into the whites, etc. But these advantages are also present in the old method, of scouring with soap.

It is true that the goods shrink when washed in an alkaline bath, which is not the case when organic solvents are used for the cleansing. It should, however, be recalled that goods which show a tendency to shrink are mostly piece-dyed goods. Such goods suffer more by dyeing on the jig than they do in washing; and much difficulty is caused by the formation of lime soaps, which is unavoidable when hard water and soap are used in the cleansing. And in this point lies one great advantage of the chemical method of scouring; that the softening of the water, which involves at least some expense, is made unnecessary. And, further, the whole of the fat or grease is extracted from the wool, and can easily be recovered.

A certain woolen mill, which was already fitted up with the apparatus necessary for chemical scouring, undertook large-scale experiments upon the chemical cleansing of certain articles with which it was dealing. First of all, delicate goods were so cleansed, and, further, such goods as, when washed in the ordinary way, would have been given only one washing and no fulling. Of course, parallel experiments with the same sort of goods from the same yarn were washed, for comparison, in the soap-soda bath as usual. It was clear, from the results, that the chemical method is not yet in a position to replace wholly the wet, soap-bath method. Certainly, a clean product is obtained, but it lacks the pleasant, soft, woolly feel. This is not due to the fact that all of the fatty material was removed by the solvent. In fact, it is perfectly possible to leave a small amount of the oil or grease in the wool, as much or as little as may be wished, by the solvent method. The cause of the unsatisfactory results rather lay in the fact that the wool extracted with the organic solvent had not undergone the swelling which is unconditionally necessary for the production of the wool-like feel of the goods.

As a colloid, wool swells in water, and still more so in alkaline baths. It is true that excessive swelling is harmful. Up to a certain point, however, swelling of the fiber is a desirable process, and forms the basis of different finishing processes, such as fixing, decatizing, etc. Through treatment with solvents, the wool fiber undergoes no swelling at all, such as is brought about in a wholesome way in the soap-bath, through the small amount of alkali set free by hydrolysis. Certainly, too extensive swelling is synonymous with damage to the fiber. According to experience, however, such dangerous swelling takes place only when the necessary care has not been observed. Normally, the wool not only does not suffer any harm through careful soaping, but actually undergoes a kind of desirable improvement in properties. Any dyer or worker in wool will confirm the statement that vat-dyed wool is of better quality than that dyed by any other method. The beneficial effect of alkaline treatment is evident.

—— • ——

Vat Dyestuffs (Anthanthrone Series)

German Patent No. 491,426 (*February* 10, 1930).—*I. G. Farben-Ind. A.-G.*—The fundamental substances in the present procedure are anthanthrone or the dinaphthyldicarbonic acids which produce anthanthrone by elimination of water. The process consists essentially in reacting such compounds with formaldehyde or substances setting free formaldehyde, in an acid solution. The products are converted to anthanthrone dyestuffs by the usual methods, in certain cases, if not already of that order; and the dyestuffs are either oxidized or dehydrogenated if necessary. If the dicarbonic acids mentioned are employed as the starting-point, the products must be subjected to treatment which will eliminate water, in order to close the rings.

The products, on oxidation or elimination of water, etc., pass into other vat dyestuffs, which are mostly toward the browns in tone. The dehydration, dehydrogenation, etc., may be of the exo or endo type. For example, if the 1-1′-2-2′-dicarbonic acid of 1-1′-dinaphthyl be condensed with para-formaldehyde or methylol-amides, scarlet to orange vat dyestuffs are formed by splitting out of water; and these products, even through mere heating with aqueous alkali, pass over, through internal dehydrogenation, to the carmine-red leuco-compounds of new reddish-brown to yellowish-brown vat dyestuffs.

Six examples are given.

New Products—Trade Notes

• COMMENCEMENT, L.T.I.

The thirty-eighth annual commencement of Lowell Textile Institute was held on Tuesday, June 9th, in Southwick Hall. Prof. William H. Timbie of Massachusetts Institute of Technology was the principal speaker. The address of welcome was given by President Charles H. Eames. He called attention to the advances in the textile world and the preparations which had been made by the graduates to enter an important field.

The medal of the National Association of Cotton Manufacturers was awarded to Emilio Gomez Moreno, Jr., of Arizona by Russell T. Fisher, representing the association. The Louis A. Olney book prize, for proficiency in the department of chemistry, went to James C. deGruchy, Jr.

Students in the department of chemistry and textile coloring who were awarded bachelor's degrees were as follows: Henry Steere Anthony, Jr., Constantine Apostolos Basdikis, James Campbell deGruchy, Jr., Roland Octave Gagnon, George Georgacoulis, Moushy Markarian, James Reynolds Redmond, John James Roarke, Bernard James Tyler, Preston Sumner Valentine, William Paul Welch, Jr., and Herbert Alvin Wormwood. Master's degrees were awarded to Albert Stephen Alcott, Jr., L.T.I., '35, and Bertil August Ryberg, L.T.I., '29.

• RESEARCH ILLUSTRATED

E. F. Houghton & Co. have recently published a 32-page booklet entitled "Research Illustrated" which deals with textile processing. Included in the table of contents are the following titles: Strict Control of Methods and Materials Is Essential in Sizing Rayon Warps, Check Up Your Starches for Better Results and Lower Costs in the Cotton Slasher Room and Weave Shed, Direct Help in Direct Knitting of Full Fashioned Hosiery, and Oil and Soap Residue in Finished Woolens and Worsteds. There are numerous illustrations. Copies are available upon request.

• CAMPBELL RELEASE

John Campbell and Co. announce the following new product:

Formadine Dark Brown RB—an allied color to the Formadine Black and Formadine Blue BB. It is stated that the very small amounts of formaldehyde brown which have appeared on the market are all imported and that this is the first time that it has been manufactured in America. It is recommended by the manufacturers for the dyeing of rayon. It is said to be a true formaldehyde brown which means that the full maximum value, merit and excellent properties are obtained by after-treating it with formaldehyde. It is claimed that it has excellent fastness to washing, very good discharge properties, and is suitable for cotton skein, hosiery and all forms of rayon, particularly rayon piece goods. A circular describing its properties, showing sample swatches and giving dyeing instructions is available upon request.

• OUTING, S.O.C.M.A.

The annual spring outing of the Synthetic Organic Chemical Manufacturers Association was held at Seaview Golf Club, Absecon, N. J., June 4th and 5th, and it was reported as a huge success. Beautiful weather enhanced the event and the golf prizes which were displayed, comprising a leather brief case and various articles of sterling silver, were universally admired and coveted.

The winners of the seven blind bogie drawings were: Henry Bower, Henry Bower Chemical Mfg. Co.; Ralph E. Dorland, Dow Chemical Co.; F. M. Fargo, Jr., Calco Chemical Co.; C. A. Higgins, Hercules Powder Co.; S. C. Moody, Calco Chemical Co.; W. S. Weeks, Calco Chemical Co., and V. E. Williams, Monsanto Chemical Co. The winners of the best putts were: G. H. Kimber, Solvay Sales Corp., and W. I. Gallaher, Columbia Alkali Co. The winner of the best approach was R. N. Mulliken of E. I. du Pont de Nemours & Co., and the winner of the longest

GRADUATES OF TEXTILE CHEMISTRY AND DYEING DEPARTMENT, L.T.I.

AWARDED MASTERS' DEGREES

Albert S. Alcott, Jr., Lowell Textile Institute '35 and Bertil A. Ryberg (Right), Lowell Textile Institute '29.

drive was K. G. Osborn of Lamb & Lerch.

The attendance at the Union dinner of the Manufacturers Chemical Association and the S. O. C. M. A. was about 155, comprising members and guests of both associations.

• ASSOCIATES WITH DINGWALL

Gordon F. Macnaughton, formerly secretary-treasurer of the Herrick-Voigt Chemical Corp., is now associated with Andrew Dingall, consulting chemist, with offices and laboratories at 101 Maiden Lane, New York, N. Y.

• CONFERENCE ON SPECTROSCOPY

A conference on spectroscopy and its applications will be held at the George Eastman Research Laboratories, Massachusetts Institute of Technology, starting on Monday, July 20th, and continuing through Wednesday, July 22nd. The following is the program:

MONDAY, JULY 20, AT 9:30 A. M.

SPECTROSCOPIC ANALYSIS OF MATERIALS

W. F. Meggers, *Bureau of Standards (with B. F. Scribner)*—Absolute Spectral Sensitivity of the Chemical Elements.

G. O. Langstroth, *McGill University (with D. R. McRae)*—Studies of Phenomena in Sources for Spectroscopic Analysis.

D. Richardson, *Massachusetts Institute of Technology* — Matrix Conditions and Excitation in Sources for Spectroscopic Analysis.

O. S. Duffendack, *University of Michigan*—New Spectroscopic Sources for the Analysis of Solutions.

Mary E. Warga, *University of Pittsburgh*—Certain Industrial Applications of Spectroscopy.

MONDAY, JULY 20, AT 2:00 P. M.

BIOLOGICAL SPECTROSCOPY

G. I. Lavin, *Rockefeller Institute for Medical Research*—The Design and Equipment of a Spectroscopic Laboratory.

L. H. Flint, *United States Bureau of Plant Industry*—Critical Wavelengths of Radiation Promoting the Germination of Light-Sensitive Lettuce Seed.

J. S. Foster, *McGill University*—Application of Spectrographic Analysis to Agriculture.

E. S. Miller, *University of Minnesota*—Application of Absorption Spectra to Plant Pigment Research.

TUESDAY, JULY 21, AT 9:30 A. M.

METALLURGICAL SPECTROSCOPY

J. S. Owens, *Dow Chemical Company (with T. M. Hess)*—Developments of Quantitative Spectrographic Analysis of Magnesium Base Alloys.

D. J. Crawford, *Watertown Arsenal*—Applications of Grating Spectrographs to Routine and Research Metallurgical Analysis.*

R. A. Sawyer, *University of Michigan and Campbell, Wyant & Cannon Foundry Co. (with H. B. Vincent and A. M. Sampson)*—Methods for Spectrographic Analysis of Ferrous Alloys.

H. B. Vincent, *University of Michigan and Campbell, Wyant & Cannon Foundry Co. (with A. M. Sampson and R. A. Sawyer)*—Routine Production Control of Alloy Cast Iron by the Spectrograph.

L. Strock, *Lucius Pitkin, Inc.*—Quantitative Spectral Determination of Lithium by Means of the Carbon Arc "Glimmschicht" Method.

TUESDAY, JULY 21, AT 2:00 P. M.*

BIOLOGICAL SPECTROSCOPY

D. L. Drabkin, *University of Pennsylvania*—The Theoretical and Practical Implications of a New Graphic-mathematical Analysis of the Absorption Spectra of Complex Molecules.

G. O. Langstroth, *McGill University (with D. R. McRae and J. S. Foster)*—Quantitative Spectroscopic Analysis for Na and K in Biological Material.

T. R. Hogness, *University of Chicago*—The Determination of Equilibria Involving Hemochromogens by the Spectrophotometric Method.

C. B. Coulter, *Columbia University (with Florence M. Stone)*—The Formation of a Cuproporphyrin Compound in Diphtheria Bacillus Cultures, and the Spectrophotometric Determination of Their Biological Activity.

L. E. Gaul, *New York City*—The Diagnostic and Research Significance of a Biospectrometric Analysis.

WEDNESDAY, JULY 2, AT 9:30 A. M.

ABSORPTION SPECTROPHOTOMETRY

T. R. Hogness, *University of Chicago*—A Spectrophotometric Apparatus for Determining Absorption Spectra—with Particular Reference to Precision and Application.

Brian O'Brien, *University of Rochester*—Rapid Measurement of Spectral Energy.

Egon Lorenz, *United States Public Health Service*—Remarks on the Construction and Calibration of Photoelectric Quantum Counters.

D. L. Drabkin, *University of Pennsylvania*—The Adequacy of Present Spectrophotometric Standards.

O. R. Wulf, *United States Bureau of Chemistry and Soils*—Vibrational Absorption Characteristic of Certain Types of Molecules in Solution.

WEDNESDAY, JULY 22, AT 2:00 P. M.

GENERAL SPECTROSCOPY AND DISCUSSION

H. A. Robinson, *University of Upsala*—Excitation Conditions in Spectroscopic Sources, Especially in the Hot Spark.

W. F. Meggers, *Bureau of Standards (with C. J. Humphreys)*—Secondary Standards of Wavelength.

Free-for-all discussion of the present status of spectroscopic analysis of materials and of general questions raised by the papers of the conference.

All papers of the conference are to be limited to approximately twenty minutes, one-half hour being allotted for each paper and its discussion.

* TUESDAY, JULY 21, AT 2:30 P. M. A visit to the spectroscopic laboratories and plant of the Watertown Arsenal is being arranged for those interested in metallurgical spectroscopy. This is open only to visiting scientists of United States citizenship. Registration for this trip should be carried out on Tuesday morning.

• CONFERENCE ON COLOR

A conference on color will be held at the George Eastman Laboratories, Massachusetts Institute of Technology, starting on Thursday, July 23rd, and continuing through Saturday, July 25th. The following is the program:

THURSDAY, JULY 23, AT 9:30 A. M.

Loyd A. Jones, *Eastman Kodak Company*—The Inter-Relationship of Various Aspects of Color.

John W. Forrest, *Bausch & Lomb Optical Company* — Spectrophotometers of the Visual Type.

Herbert E. Ives, *Bell Telephone Laboratories*—The Applicability of Photoelectric Cells to Spectrophotometry and Colorimetry.

K. S. Gibson, *National Bureau of Standards*—The Accuracy of Spectrophotometry Measurements.

THURSDAY, JULY 23, AT 2:00 P. M.

J. L. Michaelson, *General Electric Company*—Some Applications of Spectrophotometry.

G. F. A. Stutz, *New Jersey Zinc Company*—The Optics of Pigmented Films.

Carl E. Foss, *International Printing Ink Corporation*—Spectrophotometric Studies of Pigmented Films.

Lester C. Lewis, *Mead Corporation*—Recent Progress on Color Problems of the Paper Industry.

FRIDAY, JULY 24, AT 9:30 A. M.

Selig Hecht, *Columbia University*—The Measurement and Basis of Color Vision.

Deane B. Judd, *National Bureau of Standards*—The Standard Observer in Colorimetry.

David L. MacAdam, *Massachusetts Institute of Technology*—Computations Involving the Standard Observer.

Francis W. Sears, *Massachusetts Institute of Technology* — Photoelectric Colorimeters.

H. P. Gage, *Corning Glass Works*—Artificial Daylight and Its Application in Colorimetry.

FRIDAY, JULY 24, AT 2:00 P. M.

Walter M. Scott, *Gustavus J. Esselen, Inc.*—The Munsell System of Color Specification.

Dorothy Nickerson, *United States Bureau of Agricultural Economics*—The Solution of Grading Problems by the Use of a Disk Colorimeter.

F. H. Norton, *Massachusetts Institute of Technology*—Color Formation in Ceramics.

K. S. Gibson, *National Bureau of Standards*—Specification of the Colors of Railway Signal Glasses.

A. W. Kenney, *E. I. du Pont de Nemours & Company*—The Industrial Significance of Color Measurements.

SATURDAY, JULY 25, AT 9:30 A. M.

M. Rea Paul, *National Lead Company*—Color Tolerances in Industry.

Deane B. Judd, *National Bureau of Standards*—Color Tolerances in Terms of Material Standards.

W. D. Appel, *National Bureau of Standards*—Color Problems of the Textile Industry.

I. H. Godlove, *E. I. du Pont de Nemours & Company*—Colorimetry in the Dyestuffs Industry, with Special Reference to Fastness.

David L. MacAdam, *Massachusetts Institute of Technology*—The Specification of Whiteness.

Deane B. Judd, *National Bureau of Standards*—The Specification of the Whiteness of Paper.

R. E. Rose, *E. I. du Pont de Nemours & Company*—The Importance of Dyestuffs Properties Other than Color Value.

GENERAL INFORMATION

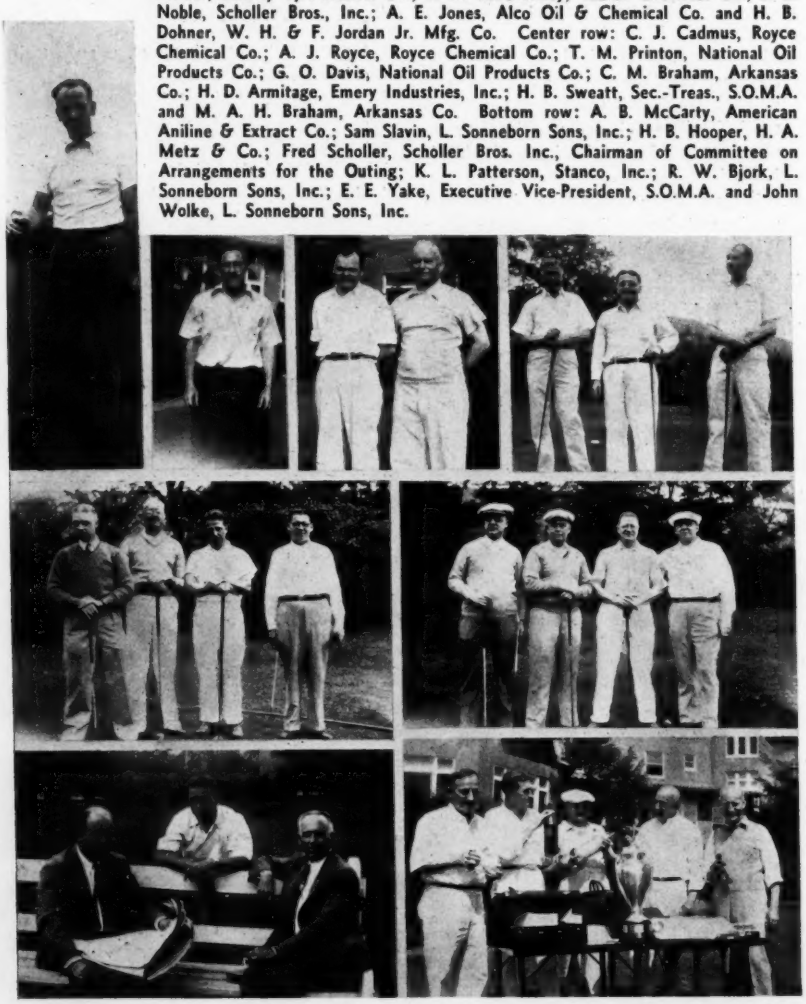
The Massachusetts Institute of Technology is located on the Cambridge side of the Charles River, approximately one mile from the various railroad stations in Boston. It is easily accessible by street car, subway, or taxicab. There will be ample free parking space on the Institute grounds for those traveling by automobile.

There is no fee for either the Color Conference or the Spectroscopy Conference. Dormitory facilities for men will be available on the Institute Campus at $4 per week. Dining facilities are available in Walker Memorial with cafeteria service, and restaurants and boarding places are close at hand.

Further information regarding the Color Conference can be secured by addressing inquiries to Professor A. C. Hardy, and regarding the Spectroscopy Conference by addressing inquiries to Professor G. R. Harrison, Massachusetts Institute of Technology, Cambridge, Massachusetts.

SULPHONATED OIL MANUFACTURERS OUTING

Photographs taken at the annual outing of the Sulphonated Oil Manufacturers Association at Buckwood Inn, Shawnee-on-the-Delaware, Pa. on June 3rd and 4th which was reported on page 339 of our June 15th issue. Reading from left to right we find in the top row: K. M. Dillabaugh, Solvay Sales Corp.; Arthur Brewer, Liberty By-Products Co., Winner of Cup for Low Net; J. M. Baeder, Liberty By-Products Co.; J. M. McChesney, Leatex Chemical Co.; J. S. Noble, Scholler Bros., Inc.; A. E. Jones, Alco Oil & Chemical Co. and H. B. Dohner, W. H. & F. Jordan Jr. Mfg. Co. Center row: C. J. Cadmus, Royce Chemical Co.; A. J. Royce, Royce Chemical Co.; T. M. Printon, National Oil Products Co.; G. O. Davis, National Oil Products Co.; C. M. Braham, Arkansas Co.; H. D. Armitage, Emery Industries, Inc.; H. B. Sweatt, Sec.-Treas., S.O.M.A. and M. A. H. Braham, Arkansas Co. Bottom row: A. B. McCarty, American Aniline & Extract Co.; Sam Slavin, L. Sonneborn Sons, Inc.; H. B. Hooper, H. A. Metz & Co.; Fred Scholler, Scholler Bros. Inc., Chairman of Committee on Arrangements for the Outing; K. L. Patterson, Stanco, Inc.; R. W. Bjork, L. Sonneborn Sons, Inc.; E. E. Yake, Executive Vice-President, S.O.M.A. and John Wolke, L. Sonneborn Sons, Inc.



• COAL-TAR DYES
Exports and Imports

Since the beginning of the current year United States foreign trade in coal-tar products has been characterized by substantial increases in exports of dyes, stains, colors and similar products while imports of such materials have declined, according to C. C. Concannon, Chief of the Commerce Department's Chemical Division.

The total value of coal-tar products exported during the first four months of the year aggregated $5,313,050 against $4,477,305 in the corresponding months of 1935. Colors, dyes, stains, and color lakes accounted for $2,545,000, or almost half the total value of all types of coal-tar products exported during the first four months of the current year, and represented a value increase of more than $400,000 compared with the corresponding months of last year, it was stated.

Analysis shows that while Japan, China, and Canada, are outstanding foreign markets for United States coal-tar products—the three together taking more than half our total exports of such products—substantial shipments are also made to a number of other countries, including British India, the United Kingdom, Belgium, Germany, Mexico, Argentina and Brazil, Mr. Concannon stated. Coal-tar dye products were shipped to 46 countries during April.

Imports of coal-tar products into the United States during the first four months of the year were valued at $4,133,350 compared with $4,946,000 during the corresponding period of 1935. Receipts of colors, dyes, stains, color acids and color bases accounted for $1,528,000 of the total, a value decline of $540,000 from receipts during the first four months of 1935. As usual our imports of such products came largely from Germany and Switzerland, with smaller quantities originating in France, the United Kingdom, and elsewhere, it was stated.

Other coal-tar product imports during the four-month period of this year included 11½ million gallons of creosote oil valued at $1,243,000; other crudes, $566,700; intermediates, $681,000; and medicinals, $25,000, statistics show.

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answer

36—I would appreciate a method in which to overcome sleaziness in chiffon silk hosiery, if any.—J. L. P. W.

Answer:— If there is a method to overcome sleaziness it is surely hard to find. Unless a seriously organized research is made, to find positively what causes it, and some radical way to do away with it, I am afraid sleaziness, more or less of it, will always be with us. It disappears at times and like the measles and the flu, comes back to plague the knitters, the dyers and the finishers, and make the day hideous and the night sleepless for them.

There was a time when it was blamed on the dyer altogether. Like everything else that went wrong with textiles, sleaziness was laid at the door of the dyer, to let him worry over it, until after much arguing and resenting it was conclusively proved that sleaziness was mostly in the goods even before they reached the dyehouse. Then the dyer was blamed for not taking it out. The conclusion was finally drawn that, by putting the blame where it did not belong, sleaziness could not possibly be eliminated. Since then it has been remedied to a great extent, but not entirely overcome. Like an epidemic of disease, if not strictly controlled it will come back.

The manufacturers of the Reading Full-fashioned Knitting Machines, of Reading, Pa., have issued a pamphlet devoted to sleaziness, its causes and prevention, that is quite instructive and interesting, especially to dyers. It states that of 13 sources liable to cause sleaziness only one can be ascribed to dyeing. That one is so obvious that I am sure any dyer with ordinary common sense would recognize it himself and avoid it, without having it pointed out to him.

For the benefit of J. L. P. W. I will take the liberty of quoting from this pamphlet what the causes are, according to Reading, hoping it will be of help to our contributor, if he is not a dyer, and to gladden his heart if he is.

"Sleaziness is defined as irregular, uneven shaped loops and presents one of the greatest difficulties in knitting satisfactory full-fashioned stockings. How to prevent sleazy knitting is a problem that is constantly before the manufacturers of this type of merchandise . . .

"Sleaziness may be caused at any point in the manufacture of the stocking, from the throwing of the silk to the last operation in finishing, and it is impossible to determine by examination just what the cause is; therefore we may outline the causes as follows:

1. Uneven silk.
2. Improper winding.
   (a) Non-uniform tension.
   (b) Winding solution.
   (c) Improperly conditioned.
3. Incorrect yarn tension on knitting machine.
4. Dirty felts and moistening troughs.
5. Running dry silk.
6. Rebounding of sinkers.
7. Too much clearance between verge plate and sinker butts.
8. Misalignment of needle bars, sinker-heads and jack-beds.
9. Misaligned needles (to back or front).
10. Wornout sinkers.
11. Knocking over not hard enough.
12. Dyeing.
    (a) Incomplete degumming.
    (b) Too many stockings in nets.
    (c) Overworking.
13. Boarding.

"The foregoing outline gives us a direct idea as to the causes of this trouble and where it may be found during the course of manufacture. It is usually necessary to make a check of all these things in order to determine the cause of sleaziness in a particular case . . ."

Thus quoth the manufacturer of the "Reading machines." In my many years as hosiery dyer I had to stand abuses and took the blame, being lied to and lied about, because I pointed out many of the above points, as the cause of sleaziness, while they thought it was my way of dyeing and my employer had decided I was too sure of myself and refused to cooperate.

The throwster should standardize his soaking solution and adopt something to keep the silk as hygro-

scopic as possible until he delivers the silk to the knitter. The knitter should keep the silk in a conditioning room so the cones will contain the same amount of moisture from the top layer to the last layer on the cone. Then if he will check up conscientiously the points mentioned by the Reading people, much of the sleaziness will surely be eliminated.

The A B C of the dyeing is too obvious to need comments, no dyer can deny that. From my own observations he can help remove the last vestige of sleaziness by boiling-off right, and this means more than many people think. I remember once I was given strict orders to put my hosiery in the boil-off bath at the boil. Where they had got the notion that it was the best way to do it I haven't the slightest idea. Since my lot was "not to reason why" I said OK and instructed my boil-off man to say we did.

What happens to silk when it enters the boil-off bath is this: First a swelling takes place, which enlarges the thread to about twice its size. By looking at a piece of sleazy knitting under a magnifying glass the loops look spread out and crooked. The action of swelling of the gum forces the threads to expand and tighten up the knitting, forcing the loops to line up in the natural position intended they should be, until the gum is dissolved, dispersed into the soap bath and the swelling is reduced, leaving the thread smaller and clean of the gum. Unless the loops are all twisted in every direction they will stay straight in the vales, serrated (closely lined up), and the longer they remain in that position a better chance they have to straighten and remain that way, which means less sleaziness will be in the knitting.

That being the case, if the goods are put in the boil-off bath at about 130° F. and gradually brought to the boil, that lot has a better chance of coming out perfect, and free of sleaziness, than if the goods had been put in at the boil and the gum removed as quickly as possible. If I am wrong I stand corrected, but it has to be proven. I did some experimenting, too.

A prolonged boiling in the dyeing bath will have a tendency of bunching and twisting the hosiery, strangling it and pulling it out of shape, which naturally will not help the hosiery any, but if there is no sleaziness in the hosiery in the first place, there wouldn't be much in it after it is dyed.

The boarders on the other hand can do much to help a sleazy lot get by, if not thoroughly freed from it, good enough to pass inspection. By leaving a bit more moisture from the finish bath, when pulled on the boards the hosiery will not dry too rapidly. The boarder then can with a piece of soft, wet cloth, lovingly and with care, smooth out a great deal of distorted stitches to make the hosiery presentable. It can be done by using persuasion and demanding cooperation.—Noel D. White.

New Question

37—I would appreciate information for positive identification of mildew on wool.—**L. D.**

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

POSITION WANTED: By salesman who covered Philadelphia territory on oils, finishes, soaps, tints and dyes. Available at once. Write Box No. 903, American Dyestuff Reporter.

CHEMICAL ENGINEER, 30, 8 years experience, 2 years Du Pont Dyeing Laboratory, wishes to enter dyehouse. Initial salary no object. Write Box No. 907, American Dyestuff Reporter, 440 Fourth Ave., New York, N.Y.

WANTED: Salesmen covering Middle West and South, representing New York Dyestuff concern. Reply stating full particulars. Box No. 908, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

SALESMAN Wanted to cover southern territory by manufacturer of sizing materials, chemical specialties and dyestuffs. Applicant must be established in the trade and have knowledge of sizing, finishing and dyeing. Address Box No. 909, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED: Chemist, recent college or technical school graduate with one or two years experience in piece dyeing cotton, rayon and mohair—cross and union. Capable of testing dyes; developing formulae and methods; and effecting cost reductions. State full particulars—age, salary desired, training and experience. Send photograph. Box No. 910, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

COLOR MATCHER—required for printed rayon, cotton and acetate piece dye. State age, experience and references. Only expert matchers need apply. Apply Box No. 911, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

SALESMAN: to sell well known and advertised line of textile oils, finishes and sizes, in New England section. Must have following. Advise territory covered at present. Write Box No. 912, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

A REAL OPPORTUNITY FOR THE RIGHT MAN
See page XII